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1963

SovietRxiv

Figure 1

Figure 1: Figure 1

Abstract

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PHYSICAL CHEMISTRY

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PHOTOREACTIONS OF Mg-PHTHALOCYANINE WITH A COORDINATED URANYL CATION

In previous communications ([1-3]) the phenomena of transfer of excitation energy from the coordinated cation UO_2^{2+} in its complex with metal-free phthalocyanine (H_2Pc) and in binary solutions $MgPc + UO_2^{2+} \cdot 6H_2O$ (nitrate) were considered. The present communication gives the results of a study of photoprocesses in binary solutions between the indicated components, occurring over time under irradiation.

Irreversible photoreaction. Binary solutions of MgPc (10^{-5} mole/l) and $UO_2^{2+} \cdot 6H_2O$ (10^{-3} mole/l) in pyridine (acetone, ethanol) were irradiated in air with a PRK-4 lamp through a UFS-4 light filter, transmitting

Fig. 1. *a* –photocomplex formation of MgPc with $UO_2^{2+} \cdot 6H_2O$ (nitrate) in a pyridine solution under the action of light ($\lambda_v = 366\,m$, $T = 290°K$); *b* – photquenching of MgPc luminescence in the presence of uranyl nitrate hexahydrate in a pyridine solution ($T = 290°K$) upon photoexcitation of only MgPc.

the region 340-390 mμ. During illumination at room temperature a gradual, rather rapid decrease in the intensity of the red fluorescence of MgPc (675 mμ), excited by the same light and recorded through a KS-17 light filter or on an ISP-51 spectrograph with an FEP-1 photoelectric attachment at a slit width of 0.1 mm, isolating a range of 1-2 mμ, is observed. Cessation of irradiation stops the decrease in intensity (Fig. 1a). It can be traced that the luminescence intensity of uranium also decreases irreversibly. The rate of this photoreaction increases with increasing uranium concentration, and at a component concentration ratio of approximately 1 : 1 (10^{-3} mole/l) the drop in intensity occurs within several seconds. Simultaneously with the decrease in intensity, the formation of an insoluble precipitate is observed; its luminescent properties, if it is dissolved in dioxane, are analogous to the properties of the synthesized complex UO_2Pc described in work ([1]). Evidently, the observed photoreaction consists in the formation between the excited (triplet) uranium molecules and the MgPc molecules of a complex of similar nature in the final product.

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

Reversible photoreactions.

When the indicated binary solution is illuminated in air with the light of a 500 W incandescent lamp through an KS-10 light filter, absorbed only by MgPc and causing its fluorescence, a decrease of the latter during irradiation is also observed. However, in contrast to the preceding result, after irradiation is stopped the initial luminescence intensity is reversibly restored (Fig. 1b). Alternation of irradiation and darkening can be carried out several times without substantial change; the phenomenon occurs only in the presence of uranyl and is observed in ethanol and acetone at component concentrations of MgPc 10^{-5} mol/l and uranyl 10^{-3} mol/l. Under these conditions only MgPc is excited; the coordinated uranyl cation in the ground state reacts with it, i.e., quenching of luminescence occurs at a rate comparable with that of the reverse dark process. Such rapid reversibility of the reaction is compatible with the presence of an electron-exchange process. The uranyl cation, having an electron affinity in solution of about 0.06 eV, is capable of removing an electron from an excited MgPc molecule even in its triplet state, the energy deficit being compensated by the solvation energy of the formed ion $MgPc^{+}$ and of the cation UO_2^{2+}, which has decreased its charge.

Fig. 2. Microphotogram of the luminescence spectrum (λ_{exc} = 366 mμ) of a binary solution of MgPc and uranyl nitrate hexahydrate in ethanol, on which only the presence of the 520 mμ absorption band is manifested: *a*—290°, *b*—77° K.

Upon photoexcitation in air of a binary solution of MgPc+$UO_2^{2+} \cdot 6H_2O$ (nitrate) in ethanol at low temperature (90° K) with the light of a SVDSh-250 mercury lamp through a UFS-4 light filter, a gradual disappearance of the luminescence and of the pigment absorption spectrum in the red region (696 mμ) and the appearance of an absorption band at 530 mμ were established (Fig. 2). It is known that in the reversible photoreaction of reduction of MgPc by ascorbic acid and other typical reducing agents, a hydrated form with the same maximum at 520-530 mμ is formed ([4]). Ethanol is not directly capable of serving as a reducing agent in this photoreaction. However, uranyl is a very active photosensitizer of hydrogen transfer from a number of acids to readily reducible dyes. It may be assumed that the uranyl ion is capable of photodehydrogenating ethanol with subsequent transfer of hydrogen to MgPc. Then the 530 mμ band should not appear in such solvents as pyridine, which are not typical photodehydrogenated molecules in sensitized photoreactions.*

Fig. 3. Photoelectric recording of the absorption spectrum at 290° K of so-

Fig. 4

Figure 4: Fig. 4

lutions in ethanol: *a*—MgPc, *b*—MgPc + $UO_2^{2+} \cdot 6H_2O$ (nitrate), *c*—MgPc + ($UO_2^{2+} \cdot 6H_2O$) (nitrate).

Photoinduced cleavage of a proton from $UO_2^{2+} \cdot 6H_2O$.

In order to detect the presumed intermediate forms formed upon illumination of the binary solution under study, recordings of the absorption spectrum of a solution of MgPc (10^{-5} mol/l) + $UO_2^{2+} \cdot 6H_2O$ were made on a DFS-4 photoelectric spectrophotometer

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* Another explanation is that the 530 mμ band characterizes the monovalently oxidized ion $MgPc^+$, similarly to sulfonated $CuPc^+$ ([5]). In that case it must be assumed that photoexcited $UO_2^{2+} \cdot 6H_2O$ (U^{6+}) removes an electron, turning into the cation U^{5+}, followed by return of the electron, and not of hydrogen, to the $MgPc^+$ ion.

(nitrate) (10^{-3} mol/l) in ethanol under additional cross irradiation. Illumination of the solution in order to obtain the absorption spectrum was carried out with an incandescent lamp (300 W), the light of which was filtered through a red light filter KS-10, absorbing wavelengths shorter than 600 mμ in order to prevent excitation of uranyl, which has an absorption band with a maximum at 430 mμ. In Fig. 3, *a* shows the absorption band at 670 mμ of MgPc obtained in this way in the absence, and curve *b*—in the presence, of $UO_2^{2+} \cdot 6H_2O$ of the indicated concentration*. The second curve (*b*) differs from the first by the presence of a weak absorption maximum at 700 mμ. With the illumination conditions maintained, the volume of solution was subjected to additional cross irradiation with focused light from an SVDSH-250 mercury lamp through a light filter selecting the group of lines at 436 mμ, which falls in the first absorption band of $UO_2^{2+} \cdot 6H_2O$ and does not affect MgPc ([2]). The absorption curve *v* (Fig. 3) obtained in this case reveals a high maximum at 700 mμ, which disappears if the additional irradiation is stopped. The reversible phenomenon described can be repeated many times in the same manner, indicating complete reversibility of the process. In the ethanol solution frozen at 77°K this phenomenon is also reproduced, but the 700 mμ maximum in it retains appreciable height even without additional excitation of uranyl (Fig. 4). In contrast to 290°K, here the photoinduced absorption band at 700 mμ does not disappear after the illumination is stopped**.

Fig. 4. Photoelectric recording of the absorption spectrum of solutions in ethanol at 77°K: MgPc + $UO_2^{2+} \cdot 6H_2O$ (nitrate): *a*—without excitation of uranyl, *b*—uranyl excited (λ_v = 436 mμ)

The 700 mμ absorption band closely adjoins the 703 mμ luminescence band observed in the luminescence spectrum of MgPc photosensitized by the uranyl ion under selective excitation of the latter ([2,3]). The common nature of these bands is proved by the fact that, when the solution is illuminated by a narrow region at 700 mμ, isolated from the spectrum of the incandescent lamp by the corresponding interference light filter, a 703 mμ luminescence band appears, belonging to the $MgPcH^+$ ion, as the preceding study showed ([3]). The increase of the 700 mμ maximum belonging to the protonated form $MgPcH^+$ under selective photoexcitation of $UO_2^{2+} \cdot 6H_2O$ is especially significant at 77°K. The absorption (700 mμ) and luminescence (703 mμ) bands of protonated MgPc are indicators of changes in the pH of the medium. At 77°K the concentration of $MgPcH^+$ is already large, and therefore photodetachment of protons and their addition to solvent molecules and MgPc does not produce so striking an effect. The simultaneous growth under these conditions of the absorption maximum also of unprotonated MgPc molecules (Fig. 4) is puzzling. It may be caused by heating of the solution by powerful focused light, leading to thermal dissociation of the hydrogen bond of MgPc with protonated H_2O molecules of the hydrate shell ([3]). A slow photoreaction of intermolecular proton transfer upon excitation by light of the protonated component of the hydrogen bond at low temperature is known. Also known are considerable changes in the constants of acid–base equilibrium experienced by aromatic amines and phenols in the excited state during the short time of their existence, as compared with the normal state of the molecule. Apparently, an analogous phenomenon occurs here as well. It is quite possible upon excitation of co-

* The curves obtained give a decrease in transmittance, not corrected for the spectral distributions of the source and the photocell.

** In the luminescence spectrum of MgPc in a binary ethanol solution with uranyl, excited at 366 mμ, distinctive dips are observed at 77°K, indicating the presence, alongside the luminescence maximum at 700 mμ, also of the 530 mμ maximum assigned above to the photohydrated form of MgPc.

of the coordinated ion UO_2^{2+}, the protonated H_2O molecules split off protons, transferring them to MgPhc molecules, which function as bases. After illumination is stopped, $MgPhcH^+$ give the protons back, and the proton-dissociation constant of uranyl hexahydrate assumes its initial value. At 77°K, owing to the absence of diffusion, this reverse process is arrested.

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Received
5 VIII 1963

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