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PHthalOCYANINE + QUINONE + WATER - PHOTOSYNTHETIC MODEL SYSTEM FOR SOLAR ENERGY
CONVERSION

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One of the ways of solar energy conversion is the modelling of separate elementary stages of natural photosynthesis.

The substance, capable to induce chemical transformations of reagents after the absorption of light by entering repeatedly in intermediate chemical interactions and, if possible, regenerating its structure after each cycle - photosensitizer (photocatalyst), - is the obligatory element of any system for water photochemical decomposition under the light of optical range. Heterogeneous systems adsorbate-adsorbent and three-component schemes of water photodissociation, consisting of sensitizer, electron carrier and electron donor have certain advantages.

The overwhelming majority of accomplished systems of photocatalytic water dissociation has certain disadvantages - the low quantum yield, the existence of expending reagents and the necessity of applying a special catalyst of hydrogen emission (usually - a highly expensive platinum).

The most perspective photosensitizers of water decomposition now are porphyrins, phthalocyanines and their complexes with metals that are synthetic substitutes of the natural sensitizer - chlorophyll.

The important features that mark out phthalocyanines (synthetic tetrapyrrol pigments of porphyrin series) among the other dyes - high photo- and thermostability, existence of characteristic absorption and fluorescence spectra in the red region of spectrum, ability for reversible redox reactions (phthalocyanines can be electron acceptor as well as electron donor, that depends on the properties of surrounding molecules).

We suggested and investigated the photosynthetic model heterogeneous system, consisting of phthalocyanine (Pc), p-benzoquinone (Q) and water, adsorbed on silica (SiO_2).

Our main experimental principle (usual principle of Terenin school) is: to carry out all experiments of photochemical and spectral investigations as purely as possible without any undesirable contacts of adsorbed molecules with outside molecules. All this required the effective purification of adsorbates as well as adsorbents, and the series of measures, preventing the contamination of samples during the investigation process.

As the adsorbents we used different kinds of silica: silica gel (specific surface about $660 \text{ m}^2/\text{g}$), silochrom (surface about $210 \text{ m}^2/\text{g}$), platinum silochrom (5 - 15 %), alumogel. Two methods of Pc adsorption were used - from gas phase and from the solution, the both were recognized to be equivalent.

The photoreactions of the photosensitized water decomposition were carried out in non-oiled vacuum reactor. The vacuum unit is assembled of standard elements (valves and nitrogen traps of stainless steel). Vacuum (10^{-4} - 10^{-5} Pa) was obtained with the help of two vacuum pumps of magnetic discharge (NORD type).

For the irradiation of the samples (depending on the necessary spectral interval) the mercury ultraviolet lamps of superhigh pressure, xenon lamps and halogen incandescent electric lamp were used. The necessary regions of spectrum were reduced by standard glass filters.

Mass-spectrometric measurements were carried out with the help of mass analyzer of ion-resonance type (IPDO-2A).

Absorption and transmission spectra of solutions and low-transparent samples in UV and visible regions of spectrum were registered with the help of two-beams prismatic spectrophotometer Specord UV VIS, and the spectra of diffuse reflection of non-transparent assays with the help of Beckman UV-5270. The spectral-computing complex KSVU-23M was also applied in the experiments. Luminescence spectra and excitation spectra were registered at spectrofluorimeters Neva, Hitachi-850 and MPF-4.

EPR spectra were registered at the serial EPR spectrometer RE-1306, modernized for the irradiation of assays in the resonance cavity and at the EPR spectrometer Bruker type.

The absolute quantum yield was measured by the method, allowing to eliminate non-controlled light losses on reflection. For this purpose the cuvette, which is the analogue of perfect absorber (investigated heterogeneous system played the role of its walls), was used.

Molecular hydrogen formation was observed under the simultaneous illumination of MgPc + Q + H₂O system, adsorbed on SiO₂, by the light with wave lengths of 300 - 400 nm and 600 - 700 nm (the reaction proceeds at light of only 300 - 400 nm region, but the output of H₂ is in 2 order less than at light of two regions simultaneously).

In special experiments with the intensity of irradiating light and temperature changing it was stated, that it is not two-photon process via triplet state.

It was supposed that in this case the formation of dihydrogen was effected as the result of photodissociation of secondary reaction products. It was discovered, that the formation of molecular hydrogen is observed also at the irradiation of systems with some other phthalocyanines (f.e. H P_c, CeP_c, VP_c, NiP_c, BeP_c, FeP_c, AgP_c, and others).

Measuring of absorption spectra showed that the sample's spectrum differs from the superposition of some spectra of single components. The appearance of green-and-brown colour of the sample after long (dozens of hours) photoirradiation is characteristic of quinhydrone, which can be transferred thermally (at 100 C) into initial system's components - p-benzoquinone and hydroquinone QH₂. The comparative analysis of the absorption and diffuse reflection spectra before and after irradiation exposed the increasing of absorption in the region of 300 - 600 nm after irradiation (the wavelength of irradiation light is more than 300 nm) and further decrease of longwave absorption.

In comparative experiments there was confirmed the supposition that phthalocyanines with variable valency can form radical cations as a result of carrying an electron over the central metal's atom also, that increases the efficiency of the process. It is stated that the molecular hydrogen emission velocity in the systems with Ce(III), Fe(II), Ag, Sn, and Mg phthalocyanines is higher than in the systems with Ni, V, and H P_c.

The formation of radical cation P_c^{•+} and radical anion Q^{•-} in the system was determined by the appearance of EPR-signals: a narrow singlet ($H = 2 \cdot 10^{-4} T$) of P_c radical cation and singlet ($H = 7 \cdot 10^{-4} T, g = 2.004$) of Q radical anion.

In order to elucidate the Pc state on the surface of SiO₂ the comparative analysis of the spectra of the components in solutions and on the surface were held. After the Pc adsorption on chemically neutral surface of SiO₂, in the absorption spectrum the expansion of bands and shears of peaks are observed, which occurred because of the hydrogen bonds formation with the hydroxyls of the surface.

One can get the sufficient information about the state of the molecule on the surface from the luminescent spectra thanks to its high sensitivity for the nearest environment of the molecule and greater information in comparison with the absorption and diffuse reflection spectra. For the purpose of elimination of the surface itself the region of excitation was usually chosen in the region of 500 nm. In the luminescent spectra of phthalocyanine, adsorbed on SiO₂, one can see the better delivery of the longwave band in comparison with the spectrum of diffuse reflecting. Variable behavior of longwave band of Pc luminescence at different wavelengths of excitation (245, 380, 550, and 640 nm) in MPc + Q + H₂O + SiO₂ system shows the formation of MPc ... Q complexes with the absorption in the orange region of spectrum. Quinone in its own region of absorption makes screened effect on Pc, as the luminescence of Pc disappeared at the excitation in the region of its shortwave's absorption. So, Q is likely to adsorb on Pc molecule and pot on the surface of SiO₂.

In independent experiments we tested the photodecomposition of hydroquinone QH₂, adsorbed on the surface of silica, by the light with wavelengths 300 - 400 nm with H evolution (identification by mass-spectra) and p-benzoquinone formation (identification by absorption spectra). The intermediate formation of semiquinone QH[•] was confirmed by appearance of the EPR-signal at the irradiation (singlet with H = 6.10 T and g-factor of free electron). Semiquinone doesn't stabilize and EPR-signal disappears in the darkness, but during the measuring at 77 K the velocity of disappearing of QH[•] signal decreases, that is explained by little mobility of these molecules on the surface at low temperature.

In special seria of experiments it was determined, that at the consequent adsorption on SiO₂ MgPc and chloranil (fluoranil), which differ from p-benzoquinone by electron affinity, ion-radical pair is formed without any additional illumination: radical cation of MgPc and radical anion of chloranil (fluoranil). We registered the complex EPR-signals in these systems, they are the sum of two signals: singlet with H = 6.10 T and wider signal with H = 8.10 T and H = 1.10 T in the cases of systems with fluoranil and chloranil accordingly. A narrow singlet belongs to radical cation MgPc^{•+}, which is slightly extended because of the influence of the surface. The wide unstructured EPR-signal in the systems with fluoranil & chloranil was identified by us as a signal of radical anion of fluoranil (chloranil).

In this system a weak interaction between MPc (H Pc) - electron donor and p-benzoquinone (chloranil, fluoranil) - electron acceptor appears as a result of their co-adsorption on the surface of SiO₂. The charge transfer energy between electron donor and acceptor with good approximation in the case of -complexes can be expressed by the following inequality:

$E > I - E - 3.3 \text{ eV}$, where E - charge transfer complex energy; I - donor's ionization potential; E - acceptor's electron affinity.

The values of charge transfer complexes energy of Pc-Q, obtained in such a way are in satisfied accord with the experimental results for all investigated donors and acceptors.

The photodissociation of water, according to obtained data occurs in many-step process. First step is the appearance of dark complex. The next step is the absorption of red light with wavelengths 600 - 700 nm by the dark charge transfer complex Pc ... Q^{•-}, that leads to the charge separation. Radical

anion Q^- interacts with the water molecule with the formation of semiquinone QH^- and OH^- ion. At the next step two molecules of QH^- give p-benzoquinone Q and hydroquinone QH_2 , which at the absorption of the photon with wavelength 300 - 400 nm dissociates to QH^- and single hydrogen.

Besides the molecular hydrogen the evolution of CO , CO_2 , O_2 was registered in mass-spectra. The registration of considerable quantities of CO is explained by the fact, that the liberated oxygen catalytically oxidizes the carbon's admixtures, presented on the metal wallsides of the vacuum unit and on the electrodes of mass analyzer.

In the process of irradiation the velocity of evolution of the water dissociation products increases and then falls down gradually, but after the additional adsorption of water vapor on the sample is practically completely reduced. The system makes the water dissociation during the dozens of hours of summary time of photoirradiation.

The process is likely to be closed by the interaction between radical cation Pc^+ and OH^- ion with the formation of initial Pc and OH , which through the formation of peroxide H_2O_2 and its dissociation leads to the formation of the molecular oxygen.

The lower border of quantum yield of the reaction as measured by molecular hydrogen emitted without any catalytic agent is equal to $5 \cdot 10^{-4}$. The use of special hydrogen emission catalysts raises the process efficiency an order higher as minimum.

So, we created and investigated the photochemical system of water dissociation, modelling the reaction centre of natural photosynthesis.

LITERATURE

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