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CATALYSIS IN STRUCTURALLY ORGANIZED MOLECULAR ASSEMBLIES FOR NEEDS OF SOLAR ENERGY UTILIZATION*

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The problem of solar energy conversion *via* the photocatalytic water cleavage in structurally organized molecular assemblies of the type of lipid vesicle systems is discussed. The results obtained in the Institute of Catalysis on the development of efficient ways of the photocatalytic charge separation *via* electron phototransfer across the bilayer lipid membrane, as well as data on the developed catalysts of water reduction and oxidation to H_2 and O_2, respectively, are presented. Results of the studies on peculiarities of the use of these catalysts in microheterogeneous systems (micellar solutions, microemulsions and suspensions of lipid vesicles) are reported. The possibility of creation of an artifical membrane-isolated photocatalytic reactive centre for oxygen evolution from water in the internal cavities of lipid vesicles is shown, that gives rise to principal possibility to close the cycle of water cleavage by introducing the reactive center for hydrogen evolution in to the outer volume of the vesicles. The potentialities of vesicle-based systems for solar light accomplishing the closed-loop process of water cleavage under the action of are discussed.

Key Words : Charge Separation; Water Cleavage; Artificial Photosynthesis; Solar Energy

INTRODUCTION

DIRECT conversion of solar energy into the chemical energy of fuels seems to be one of the most promising ways of its utilization. Considerable interest here is shown in the photocatalytic processes of producing hydrogen and other energy-carriers from water and atmospheric gases through endergonic processes like water cleavage into hydrogen and oxygen and reduction of CO_2 and N_2 by water to hydrocarbons, alcohols, hydrazine and ammonia.[1–3] One can note that many of these reactions have already been accomplished in nature *via* plant photosynthesis, fixation of nitrogen, microbiological fermentation and methane formation. Creation of artificial photocatalytic systems for these processes could, in principle, give a basis for an inexhaustible source of resources of fuels and raw materials for energetic and chemical industries. Of special interest appears to be also production of "noble" energy-carriers such as hydrogen by the photocatalytic

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processing of non-traditional energy raw materials, specifically, some organic or sulphur-containing compounds that are wastes of large-scale chemical plants.

Of the above indicated processes the photocatalytic water cleavage seems to be the most attractive at present. Hydrogen is known to be not only a good and ecologically pure chemical fuel, but also a valuable material for chemical industry, and water is a cheap and practically inexhaustible source for hydrogen production. In addition, from the information accumulated to date about the mechanisms of chemical reactions, it may be expected that of all the energy-storage reactions, the photocatalytic cleavage of water will be the simplest one to accomplish.

Developments in the use of photocatalytic systems for water cleavage into molecular hydrogen and oxygen are already achieving successes. These systems are conventionally divided into two types : semiconductor and molecular photocatalytic systems. Substantial progress has already been gained in the development of semiconductor systems[1-3] with up to 10 per cent efficiency of solar energy convension. The main problem that hinders a wide utilization of such systems is photocorrosion of semiconductor electrodes.

Molecular photocatalytic systems are based as a rule on reproducing both the function and the scheme of natural plant's photosynthesis. For this reason, creation of molecular photocatalytic systems—chemical models of photosythesis—presents interest not only for applied needs but also for the fundamental research.

Development of photocatalytic systems for water cleavage is associated with the development of three types of mutually related catalysts :[1-3]

(*i*) photocatalysts (PhC) for charge separation, that is formation of starting re-agents for water cleavage, namely, strong reductant (A^-) and oxidant (D^+) :

$$A + D \xrightarrow[\text{PhC}]{h\nu} A^- + D^+, \qquad \ldots(1)$$

(*ii*) catalysts for subsequent "dark" multielectron reactions of water reduction to H_2 by reductant A^- :

$$2A^- + 2H_2O \xrightarrow[\text{cat}_1]{} 2A + H_2 + 2OH^- \qquad \ldots(2)$$

and (*iii*) catalysts for water oxidation to O_2 by oxidation D^+ :

$$4D^+ + 2H_2O \xrightarrow[\text{cat}_2]{} 4D + O_2 + 4H^+. \qquad \ldots(3)$$

As is seen, this scheme is essentially the same as the sequence of processes that lead to light energy storage in natural plant's photosynthesis. The only difference is that in the natural photosysthesis, solar energy is stored in the form of chemical energy of carbohydrates, whereas in the photocatalytic water cleavage in the form of chemical energy of hydrogen.

The major difficulty that arises in the development of the molecular photocatalytic systems for water cleavage is to accomplish reaction (1) in such

a way that the back recombination reaction $D^+ + A^- \rightarrow D + A$ would be suppressed. This latter simple and highly exothermic reaction usually proceeds much faster than complex catalytic reactions (2) and (3). In particular, for this reason efficient photocatalytic water cleavage is difficult to accomplish at present in a simple homogeneous system.

It looks likely, that in order to overcome the mentioned difficulty molecular photocatalytic systems must contain structurally organized molecular assemblies resembling reactive centers of natural photosynthesizing "apparatus", in which particles D and A (and, consequently, particles D^+ and A^- formed during reaction (1)) are spatially separated. Such "apparatus" may be made sufficiently versatile to be used for water cleavage as well as for many other endergonic redox reactions during which light energy can be stored (for example, fixation of carbon dioxide by reducing with water, etc.).

At the present state of art, microheterogeneous systems based on microemulsions micellar solutions and lipid vesicles are considered to be the most interesting for the development of structurally organized molecular photocatalytic systems. Especially successful attempts in this field have already been made with the use of systems based on lipid vesicles. In this paper, we shall consider the most important results, obtained in our laboratory at the Institute of Catalysis, Siberian Branch of the USSR Academy of Sciences, in the development of microheterogeneous systems for the efficient photocatalytic charge separation as well as in the adjustment of these systems for "dark" catalysts, which allow one to provide processes of water reduction and oxidation.

Results and Discussion

Spatial Charge Separation

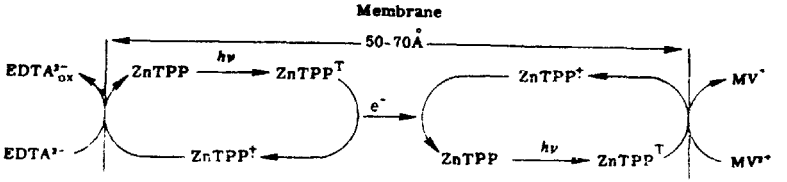
Lipid vesicles are microscopic (about 300 to 1000Å in diameter) spherical species formed by a bilayer lipid (in our case lecithin) membrane, whose inner and outer volumes could have unmiscible aqueous solutions of different composition. One solution for example, in the inner volume could have particle D while the other, for example, in the outer volume could have particle A. Thus reaction (1) in such systems has to occur *via* directed (vectorial) electron phototransfer across the membrane.

In order to achieve a sufficiently high efficiency of the systems under consideration, a rather deep insight into the possible mechanism of electron phototransfer across the membrane was indispensable.

System I—First we have done this[4] using vesicles with a water-insoluble complex, zinc(II) tetraphenylporphyrin (ZnTPP), embedded as a photocatalyst into the membrane and localized near its inner and outer surfaces. In the presence of an irreversible electron donor (e.g. anions of ethylendiaminetetraacetic acid, $EDTA^{2-}$), which does not penetrate across the membrane, in the inner volume of vesicles and of a reversible electron acceptor (e.g. methylviologen bication, MV^{2+}), which also

does not penetrate across the membrane, in the outer volume, the photocatalytic electron transfer occurs through the membrane from $EDTA^{2-}$ to MV^{2+} under the action of visible light. The quantum yield, φ, of this transfer did not exceed 0.2 per cent, like that for the analogous systems, proposed earlier (see e.g. review).[3]

Based on the detailed study of the process we have suggested the following two-quantum scheme for electron phototransfer across the membrane in system I:



Here $ZnTPP^T$ denotes the triplet excited state of ZnTPP.

As the first chemical act this scheme assumes the electron phototransfer at the outer boundary of the vesicle membrane:

$$ZnTPP^{T}_{out} + MV^{2+} \xrightarrow{<2.10^{-5}s} ZnTPP^{+}_{out} + MV^{+},$$

which is followed by the tunnel electron transfer across the membrane from an excited ZnTPP molecule located near the internal membrane surface onto $ZnTPP^{+}_{out}$;

$$ZnTPP^{T}_{int} + ZnTPP^{+}_{out} \longrightarrow ZnTPP^{+}_{int} + ZnTPP_{out} \qquad ...(4)$$

Finally, irreversible oxidation of $EDTA^{2-}$ takes place:

$$ZnTPP^{+}_{int} + EDTA^{2-} \longrightarrow ZnTPP_{int} + \text{products of } EDTA^{2-} \text{ oxidation.}$$

The process (4) seems to be the rate-determining step for this scheme.

These data together with the results of our study of photochemical charge separation in "water in oil" microemulsions have allowed us to propose several ways to improve that efficiency of electron transfer across the lipid membrane.[5,6]

First, we have tested a technique based on the suppression of the electrostatic field that prevents the electron transfer across the membrane. Indeed, in the process of phototransfer the internal volume of vesicle acquires a positive electric charge and its outer volume a negative one. This creates an electric field that may slow down electron transfer. To suppress this field we introduced into the membrane, along with the photocatalyst, valinomicine which is a selective carrier of potassium cations across the membrane. The simultaneous transport of electrons and K^+ cations across the membrane prevented accumulation of positive charges in the inner

volume or even created a deficiency of these charges. As a result, we succeeded in increasing the quantum yield φ of electron phototransfer across the lipid membrane by a factor of 2–3.

System II—We have succeeded in increasing the quantum yield by exploiting the following idea. Since in system I the process (4) seems to be the rate-determining step, one can try to accelerate electron-phototransfer following the example of photosynthesizing organisms. This could be done by additional excitation of the molecule of ZnTPP on the inner surface of the membrane *via* energy transfer from an "antenna," i.e. a sensitizer which accumulates light and transfers the excitation to "reactive centres" (ZnTPP molecules embedded into the membrane) in the same way as does the pull of molecules of "antenna's" chlorophyll in chloroplasts. The water-soluble *tris*bipyridyl complexes of ruthenium(II), $Ru(bipy)_3^{2+}$, introduced into the inner volume of vesicles was used as a sensitizer—"antenna". The thermodynamic properties of the excited state of $Ru(bipy)_3^{2+}$ are such that it is capable of providing not only the energy transfer to ZnTPP, but also the electron transfer onto $ZnTPP^+$ and even onto ZnTPP (which may result in the formation on the internal membrane surface of the radical-anion $ZnTPP^-$ that, in principle, also can transfer an electron onto the radical-cation $ZnTPP^+$ formed on the external membrane surface). The life-time of the electronically excited triplet state of $Ru(bipy)_3^{2+}$ (*ca.* 6.10^{-7} s) is sufficient for excited particles to collide many times with the wall of the internal volume (which are 150–220Å in diameter) of the vesicle before they are spontaneously deactivated. Our experiments indicate that the presence of $Ru(bipy)_3^{2+}$ leads not only to the spectral sensitization of the process (owing to additional light absorption by the ruthenium complex in the regions where absorption of ZnTPP is negligible) which is accompanied by approximately 6-fold increase in the rate of MV^+ accumulation, but also to a 2–3-fold increase (even if one takes into account the light absorbed both by ZnTPP molecules and by $Ru(bipy)_3^{2+}$ itself). The registered value $\varphi = (0.6 \pm 0.2$ per cent) seems to be the maximum one of values known to us for the system based on the vesicles with a photocatalyst embedded in a lipid bilayer and indicates a significant improvement of conditions for the electron phototransfer (compared to the system I).

System III—Our next step was modification of system II to develop an asymmetric (from the photochemical point of view) membrane containing a reversible electron carrier, instead of the photocatalyst, inside the lipid bilayer.[6,7] The exact composition of the system with such a carrier was selected on the basis of our experiences with systems I and II as well as of our experiments with the photocatalytic electron transfer across the interface in microemulsions of the "water in oil" type.[3] In system III, like in system II, $Ru(bipy)_3^{2+}$ was introduced as a photocatalyst into the inner volume of the vesicles. No additional photocatalyst was inserted into the lipid bilayer. As the electron carrier cetylviologen bication, CV^{2+}, was used. The molecules of CV^{2+} are distributed near the lipid-water interface and cannot diffuse across the membrane. As found, in the presence of an irreversible donor $EDTA^{2-}$ in the inner volume, the electron transfer from $EDTA^{2-}$ onto the CV^{2+} particle, located near the inner surface of the vesicle, occurs under illumination. The radical

cation CV^+ formed appeared to be capable of transferring its "excess" charge across the membrane *via* two different mechanisms : by *trans*-membrane diffusion of the CV^+ particle itself and by long-distance tunnel electron transfer onto the CV^{2+} bication located on the external wall of the membrane. The study of the rates of these two transfer processes across the membrane has shown that the tunnel transfer is much faster than a diffusion one, the characteristic transfer times being respectively *ca.* 0.2 and 2.5s. In the presence of an appropriate acceptor such as the $Fe(CN)_6^{3-}$ anion in the outer volume, the "excess" electron of the CV^+ particle can easily be transferred onto this acceptor. In this case, the quantum yield of electron phototransfer across the membrane can be increased up to 15 ± 5 per cent. The most important reason for the large value of φ is here a high frequency of collisions of excited particles of $Ru(bipy)_3^{2+}$ with the inner surface of the acceptor-containing membrane (or even their adsorption on the membrane) and, consequently, a low probability of useless deactivation of the photocatalyst. In fact, inversion of system III, in other words, exchange of the contents of the dispersed and bulk water phases leads to a more than 100-fold decrease in φ due to the lowered efficiency of electron transfer from the excited photocatalyst to CV^{2+}.

Thus, the attempts to increase the quantum yield of electron phototransfer across the bilayer lipid membrane have resulted in developing quite efficient photocatalytic systems to receive rather strong oxidant and reductant separated by the membrane. These achievements allow one to start researches on combination of the structurally organized systems for the photocatalytic charge separation with the catalyst for "dark" processes (2) and (3) in order to reduce or oxidize water to hydrogen and oxygen, and, finally, to create a system with the closed cycle of water cleavage, that is an artificial photosynthesis system.

Fig. 1 gives a comparison of redox characteristics of intermediate species that participate in electron phototransfer in systems I, II and III. The scheme in Fig. 1 shows also the redox potentials for hydrogen and oxygen evolution from water at *p*H7 (E is respectively -0.4 and $+0.8$V against N.H.E.).

Note that the scheme of electron phototransfer in systems I and II is quite similar to the "*Z*-scheme" of photosynthesis in plants, while this scheme in system III resembles the scheme of charge separation and electron transfer in *n-p*-junctions of semiconductor solar cells.

It can be seen also that in all the systems the electron phototransfer produces particles which are capable (as far as their thermodynamic properties are concerned) of both reduction of water to hydrogen (radical cations of viologens) and of oxidation of water to oxygen (radical cation $ZnTPP^+$ and complex $Ru(bipy)_3^{3+}$). It makes in principle possible to accomplish the closed cycle of water cleavage in systems I–III by introducing therein suitable catalysts for the dark processes (2) and (3).

Catalysts for the "Dark" Processes of Water Reduction and Oxidation

A lot of catalysts for reaction (2), that is hydrogen evolution from water under the action of one-electron reductants, have been developed by the moment.[1–9] Good

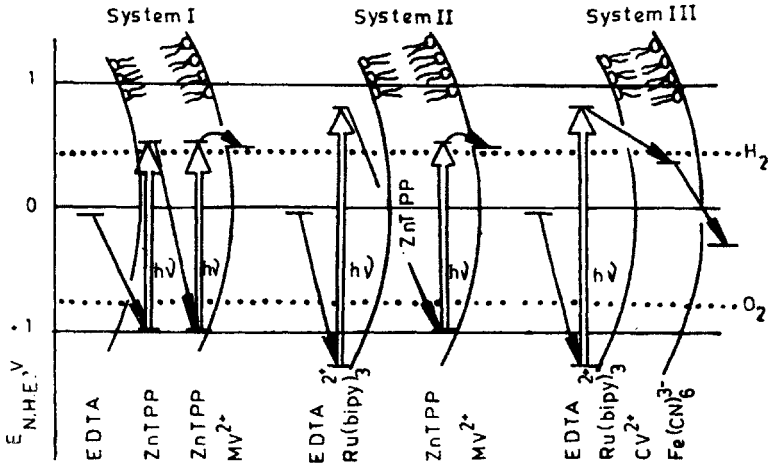


FIG 1 Energy diagram of the chains of electron phototransfer across the lipid membrane at *p*H7 on the scale of redox potentials.

catalysts for this reaction are colloidal and finely dispersed, free or stabilized, metals both noble (Pt, Rh, Pd, Au, Ag, etc.) and non-noble, in particular, Cu, Cd and, probably, Ni. Of great interest are heterogeneous catalysts, in which small metallic particles are anchored on inorganic and polymeric supports. Enzymes—hydrogenases, which provide hydrogen evolution or its consumption in metabolism of a number of microorganisms and which are now a days the most active catalysts for reaction (2), have also been known for a long time. Recently, a broad class of homogeneous catalysts for hydrogen evolution from water has been found; these are *iso-* and *hetero-poly* compounds of tungsten and molybdenum. Also, some cobalt complexes with macrocyclic ligands were reported to provide homogeneous catalysis of reaction (2).

Methods of preparation of many catalysts for the hydrogen evolution from water are quite simple. For example, the most comprehensively studied heterogeneous catalyst,[10] based on finely dispersed metallic rhodium stabilized on amine-containing polymers, is prepared by a mild reduction of polymeric Rh(III) complexes of amine type in aqueous media by V^{2+} and Cr^{2+} aquacations. Finely dispersed rhodium particles (*ca.* 10–20Å) chemically bound with the polymeric support serve as active component of this catalyst.

An important advantage of catalysts supported on polymers is their stability in aqueous solutions over a wide range of *p*H. In addition, these catalysts can be prepared in the form of granules or films, including optically transparent films, with the controlled geometric characteristics.

For the most active and stable rhodium catalysts supported on granulated AN—221 anionites, the activity per unit mass can exceed 0.5mol H_2/g catalyst hr, whereas for natural enzymes hydrogenases, that are also known to serve as catalysts

for reaction (2), it ranges at 0.2–200mol H_2/g enzyme hr. Being inferior to hydrogenases by the activity per unit mass, rhodium-polymeric catalysts are more stable than these enzymes, especially in acid media. Moreover, the activated catalysts can be stored in air for a year or even longer period without noticeable losses of the activity.

A high catalytic activity in reaction (2) was observed for polymeric complexes of ruthenium as well as of platinum and palladium. The activity of the polymeric complexes containing non-noble metals (copper, for example) can be nearly the same as that of catalysts based on noble metals. This fact may be of sufficient importance for future applications of metal-polymeric catalysts in hydrogen-producing photocatalytic systems of practical interest.

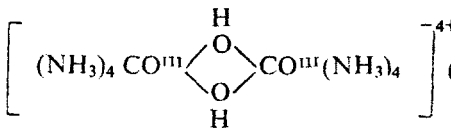
In contrast to the above-mentioned catalysts for hydrogen evolution from water, many of which had been known for a long period before the researches on photocatalytic water cleavage were initiated, the first artificial catalysts for water oxidation to oxygen by mild one-electron oxidants (reaction (3)) were found only at the end of 70s. Those were heterogeneous oxides of some transition metals (the most active catalyst of this type appeared to be RuO_2) and homogeneous as well as microheterogeneous catalysts based on some compounds of metals like iron, cabalt and copper.[1–9] In particular, we have found[9] for reaction (3) a set of homogeneous catalysts, based on partly hydrolyzed complexes of cobalt, iron and copper or on water-soluble porphyrins and phthalocyanins of the same metals, as well as of heterogeneous catalysts based on mixed hydroxides of transition metals and oxides of the spinel type.

One of the most specific features of the artificial catalysts of reaction (3) is the selectivity of their action, in other words, their ability to direct the strong oxidant D^+ towards reaction (3) but not toward other possible side processes of oxidation, e.g. of organic compounds, which can be present in the solution, or even of the ligands of the complex-oxidant itself.

Electro- and photo-chemical properties of ruthenium complexes with ligands of bipyridyl and phenanthroline type allow one to consider these complexes as promising candidates on the role of photocatalysts, whose oxidized form could serve further as particle D^+ in reaction (3). Therefore, the main part of researches on the development of catalysts for reaction (3) has been performed using these complexes.

With $Ru(bipy)_3^{3+}$ used as oxidants D^+, the activity and selectivity of homogeneous catalysts of reaction (3) were found to depend upon many factors and primarily upon the nature of catalysts, their concentration and *p*H of the medium. A highly selective oxidation of water to oxygen appeared to be achieved only in exceptional cases; as a rule of selectivity of the catalyst action does not exceed 70–90 per cent (in terms of the equation (3)). The remainder D^+ particles provide an oxidation of organic compounds present in the solution, including bipyridyl ligands of the oxidant itself; in some cases these side-processes are accompanied by

the evolution af CO_2, which is the product of a complete catalytic oxidation of organic molecules.

The mechanism of O_2 evolution is still far from being clear both for homogeneous and heterogeneous catalysis. However, some mechanistic features of this process have already been revealed. Note first that numerous data seem to indicate that for homogeneous complexes with simple ligands these are hydrolysed forms that are responsible for the catalytic activity. Moreover at least in some cases these hydrolyzed forms seem to be binuclear species, like e.g. amine binuclear complex  (see ref. 9). Sometimes hydrolyzed forms of cobalt-, iron- or copper-containing compounds can produce catalytically active oligomeric or even microheterogeneous particles. As well, there are some evidences[9] indicating a possible catalytically-important role of bi- or oligomeric forms of water-soluble phthalocyanins containing a reversibly oxidized macroligands in the process of O_2 evolution.

Catalytic properties of heterogeneous catalysts of reaction (3) were examined[9] using spinels (which are mixed oxides with the general formula $M_1^{II} M_2^{III} O_4$, where M_1^{II} and M_2^{III} are respectively di- and trivalent metal atoms) or mixed hydroxides of non-noble metals. The selectivity of action of the best heterogeneous catalysts based on cobalt- or iron-containing compounds of the discussed types is the same as that of the best homogeneous catalysts of reaction (3).

It is of special interest, that for the catalysts based on mixed cobalt and iron hydroxides a promoting effect (increase in selectivity) of various additives such as Ce^{4+}, Sn^{4+}, Al^{3+} and other redox-inactive cations has been found. The variations in the catalytic properties under the action of promoters seem to be induced by the entrance of the promotor cations into the reaction centre of the heterogeneous catalyst (possibly, surface-centered multinuclear hydroxostructure) and the subsequent changes in the acidity of protons of OH-groups which are coordinated to the ions of the "basic" redox-active metals.

Heterogeneous catalysts are almost as selective as homogeneous catalysts, but are typically more stable.

Conjugation of Photochemical Charge Separation with the Steps of Water Reduction and Oxidation in Micro-Heterogeneous Systems

It should be especially noted that the all above-described catalysts for oxygen and hydrogen evolution from water have been tested and studied only in the situation, when particles A^- and D^+ together with the catalysts were introduced into the homogeneous aqueous solution. At the same time one should expect that some

peculiarities concerning both activity and selectivity of the catalysts' action can arise when using these catalysts in the microheterogeneous systems discussed above. In the particular situation of reactions (2) and (3), these peculiarities can be caused by the following reasons : (*i*) in order that these reactions should occur one should create the conditions allowing either localization of particles A^- and D^+ in the same phase (water or hydrophobic) with the suitable catalyst or arranging a transfer of these reactants to each other (or even the creation of a special electron-transporting chain to initiate the action of redox catalysts, as it is done in photosynthesizing organisms); (*ii*) electrostatic and hydrophobic interactions with the interface of the microheterogeneous system can be expected to lead to an unfavourable mutual orientation or mobility of the reagents and the catalysts, that can affect strongly the occurrence of reactions (2) and (3) near the interface; (*iii*) the same interactions can, in principle, change the structure or the properties of the catalytically-active centre in an unfavourable way (in comparison with homogeneous water solution) or even destroy it; and (*iv*) organic compounds that form microheterogeneous systems can be involved in reactions (2) and (3) by competing with H_2O or H^+ and OH^- particles, needed to create the final products of water reduction and oxidation. This latter fact imposes particular requirements on the selectivity of the catalysts used in microheterogeneous systems.

In order to choose catalysts that are appropriate to accomplish reactions (2) and (3) in microheterogeneous systems (or, in other words, to create the catalytically-active centres adjusted to these systems), we have begun the study of these reactions in "sacrificial" systems, which are widely used either for hydrogen evolution from water (provided that a special irreversibly consumed donor-"sacrifice", but not water, is simultaneously oxidized by particles D^+) or for oxygen evolution from water (provided that an acceptor-"sacrifice" instead of water undergoes a simultaneous irreversible reduction, e.g,, by particles A^-).

Hydrogen evolution in the outer volume of vesicles can be achieved rather easily in the case of systems I and II. In fact, the water-soluble MV^+ cation, generated in the outer volume of these systems, is known to be capable to evolve hydrogen in the presence of enzymes such as hydrogenases as well as of some of artificial catalysts. By using system I, we have demonstrated[11] the possibility of the photocatalytic hydrogen evolution in the solution of vesicles as a result of electron phototransfer across the lipid membrane (from the irreversibly oxidized $EDTA^{2-}$ in the inner volume of vesicles). As the catalysts for H_2 evolution the hydrophylic hydrogenase of *Thiocapsa roseopersicina* or the above described heterogeneous rhodium-polymeric catalyst developed in our loboratory, were used (see Fig. 2). The quantum yield of H_2 production in the situations under discussion was comparable with that of MV^+ accumulation in system I.

The photocatalytic H_2 evolution in vesicle suspensions in the absence of any electron phototransfer across the membrane was also reported;[12–15] in studies of this type all the components of the "sacrificial" system were located on one side of the vesicle's membrane (in the inner or outer volume). In these cases, the lipid

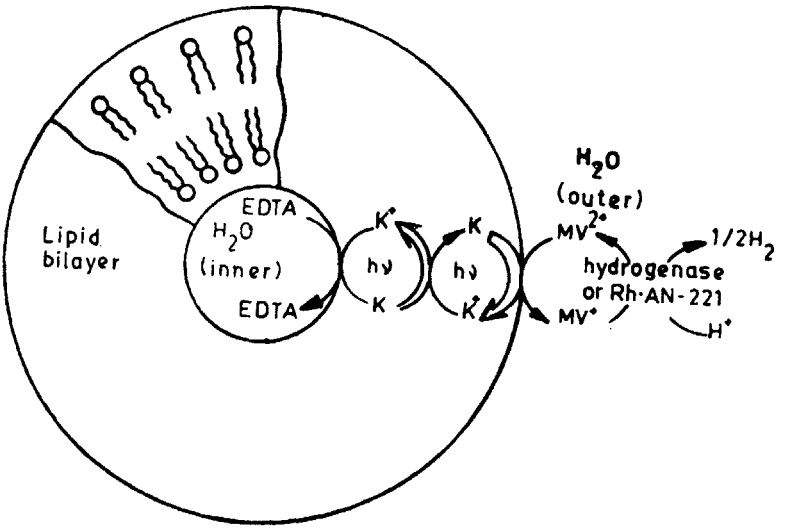


FIG 2 The photocatalytic reaction centre for hydrogen evolution in the suspension of the lipid vesicles. K denotes photocatalyst—ZnTPP.

membrane was used uniquely as a support for either a water insoluble photocatalyst[12] or a catalyst for hydrogen evoluation.[13,14] Recently, the development of photocatalytic reactive centres of hydrogen evolution in the inner volumes of vesicles has been reported,[15] clusters of metallic Pt, obtained inside the vesicles *via* photolysis of platinum compounds, playing the role of the reactive centres.

In all the above-mentioned studies only hydrophylic componds, located in one of the aqueous phases—inner or outer—of the vesicles' suspensions served as one-electron reductant A^- in reaction (2). In this case, no specific effect of the system heterogeneity on H_2 photoevolution was observed.

Nevertheless, an effect of heterogeneity was revealed when strongly hydrophobic reductants such as radical cation CV^+ in system III were used as particles A^-. In this system the particles of CV^+ do not escape from the lipid membrane into the outer bulk water phase and located inside the membrane nearby its surface. We have found that, in the presence of the hydrophylic hydrogenase of *Thiocapsa roseopersicina*, CV^+ as well as the reduced forms of the similar lipophilic viologens such as heptyloctyl- and decylviologen appeared to be much poorer specific electron donors for hydrogen evolution than methylviologen radical-cation MV^+. This is due to, first of all, the fact that strong hydrophobic interactions of CV^+ with the membrane weaken the electron-donor ability of CV^+ as compared to MV^+; indeed, in the presence of the lipid vesicles the electrochemical reductive potential of CV^+ is noticeably (by 0.24V) more positive than that of MV^+.[16] Thus the reductive potential of CV^+ is insufficient to reduce water under the standard conditions and at *p*H 7 (see Fig. 1). In this situation, evolution of a significant amount of H_2 in neutral solution is thermodynamically allowed only after almost complete (> 99 per cent) reduction of CV^{2+}, that can be achieved only with the use of the strong

irreversible chemical reductant, e.g. dithionite, and clearly cannot be achieved in the photochemical "sacrificial" system. However, even in the case of CV^{2+} reduction by dithionite, the rate of H_2 evolution, which was catalyzed by the hydrophilic hydrogenase, appeared to be more than one order of magnitude slower than in the case of MV^{2+}, for the other above-mentioned viologens the diminishing of the H_2 evolution rate slowing down monotonously with the increase of their hydrophobity. This fact is related to the existence of a correlation[17] between the rate of H_2 evolution by hydrogenase and the standard redox potential of the substrate used. Indeed, in acidic media (pH < 4) hydrogen evolution is thermodynamically allowed even at a low fraction of reduced CV^{2+}; unfortunately in such media the hydrogenase inactivation takes place. Nevertheless, we succeeded in observing photoevolution of H_2 at pH 3.5 using radical cations CV^{+} as well as the other lipophilic viologens embedded into the vesicle membranes when substituting the hydrogenase by a colloid metallic catalyst (in our case colloid Pd with the size of particles of about 70Å prepared by reduction of Pd salts with hydrogen).

Evolution of oxygen in solutions of the lipid vesicles seems to be the most difficult problem to be solved. In principle, the catalysts for this process, when using oxidant of the $Ru(bipy)_3^{3+}$ type are known (*see above* discussion). Therefore, one may hope to accomplish the photocatalytic oxygen evolution at least in systems II and III upon substitution of the irreversible donor $EDTA^{2-}$ by the appropriate catalyst. On the other hand, a large amount of easily oxidized organic compounds (lecithin and its impurities), which are obviously present in the vesicle suspensions, may result in consumption of $Ru(bipy)_3^{3+}$ for the oxidation of these compounds rather than for that of water. In fact, the addition of vesicles to a well-known homogeneous "sacrificial" system for the photocatalytic oxidation of water, namely, $Ru(bipy)_3^{2+}$–$CoCl_2$–$Co(NH_3)_5\,Cl^{2+}$, leads to a 2-fold decrease in the yield of O_2 in comparison with homogeneous aqueous solution. (Here and below by the yield of O_2 we mean the total amount of O_2 evolved in the experiment, in respect to the amount of an irreversible acceptor introduced into the system).

To examine the influence of the water-hydrophobic interfaces on the photocatalytic oxygen evolution, we began with the study[18] of this reaction in micellar solutions of sodium dodecylsulphate SDS; the solutions contained also the photocatalyst $Ru(bipy)_3^{2+}$, the catalyst for water oxidation $CoCl_2$ and an irreversible electron acceptor—$Co(NH_3)_5\,Cl^{2+}$ or $S_2O_8^{2-}$. After the electron has been transferred from the excited $Ru(bipy)_3^{2+}$ complex onto the acceptor, the strong oxidant $Ru(bipy)_3^{3+}$, which plays the role of D^+ particle in reaction (3), is formed. Owing to a strong absorption of the ruthenium complex on the surface of anionic micelles of SDS, all reactions with participation of D^+ occur at the micelle-water interface. While for $Co(NH_3)_5\,Cl^{2+}$ the kinetics of O_2 evolution in the micellar and in homogeneous solutions were nearly the same, for the acceptor $S_2O_8^{2-}$ a more than 12-fold increase in the total yield of O_2 in comparison with the same but homogeneous solutions was observed. The latter phenomenon appeared to be due to the fact that the negatively charged surface of micelles protects the ruthenium complex adsorbed thereon against the destructive action of the radical anion SO_4^{-}, which is

an intermediate product of the irreversible reduction of $S_2O_8^{2-}$. The mechanism of such protection consists in the Coulomb repulsion of SO_4^- from the photocatalyst-containing surface of micelles into the bulk solution. Simultaneously, Coulomb interactions of the reagents with the surface of micelles slow down the process of $^*Ru(bipy)_3^{2+}$ quenching by $S_2O_8^{2-}$ anions, which leads to an increase (in comparison with the homogeneous situation) in the duration of O_2 evolution which stops only when the complete consumption of $S_2O_8^{2-}$ has been achieved.

It has also been found that in the presence of $S_2O_8^{2-}$ in both homogeneous and micellar solutions, the evolution of oxygen demonstrates an autocatalytic character, that is $CoCl_2$ is not actually needed for the process to occur, because a catalyst, which seems to be the product of partial destruction of $Ru(bipy)_3^{2+}$ by the SO_4^- radical, is formed under illumination after some induction period. In the presence of $CoCl_2$ in solution, no induction period is observed in the process of O_2 evolution.

Of the top interest is to cause the photocatalytic O_2 evolution in systems II and III (Fig. 1) by arranging the process in the inner volumes of vesicles. The main difficulty arising here is due to an extremely small size (*ca.* 100Å) of the inner volume of the vesicle. Evidently, in this case one could try either to use the reported homogeneous catalysts of oxygen evolution, which should be introduced into the lipid vesicle during the process of its formation, or to organize assembling the water-insoluble catalyst from the components introduced inside the vesicles.

First we tried to create the oxygen-evolving centres for the very convenient (for providing experiments) and nevertheless adequate enough model of the inner cavity of the vesicle; as this model a water droplet of the "water in oil"-type microemulsion was exploited. We have succeeded[19] in observing the photocatalytic process of oxygen evolution in such microemulsion consisting of xylene, *n*-pentanol, SDS and water. $Ru(bipy)_3^{2+}$ and the irreversible electron acceptor ($[Co(NH_3)_4\ CO_3]^+$) were introduced simultaneously into the dispersed aqueous phase. Due to the electron phototransfer from $Ru(bipy)_3^{2+}$ to the acceptor, a strong oxidant, $Ru(bipy)_3^{3+}$ is formed, while the reduced cobalt complex decomposes to produce coordinatively unsaturated complexes of Co(II). The catalyst of water oxidation *via* reaction (3) seems to be formed inside the droplets either from the accumulated coordinatively unsaturated complexes of Co(II) (which can then be oxidized and form multinuclear associates conceptionally stated as homo- or microheterogeneous catalysts of reaction (3), (*see above*), or from the $[Co(NH_3)_4\ CO_3]^+$ complex itself. The latter version seems to be supported by the following data. First, the Co^{2+} ions intoduced into the suspension of vesicles before the illumination exhibit no catalytic activity with respect to O_2 evolution (*vide infra*), and, second, the complex $[Co(NH_3)_4\ CO_3]^+$, in which the highly labile ligand CO_3^{2-} is easily substituted by H_2O, can form dimers upon oxidation thus producing binuclear ammine complexes known to be the efficient homogeneous catalysts of water oxidation (*vide supra*). By the moment of the complete consumption of the acceptor the registered total yield of O_2 was

about 5 per cent per the acceptor used. This is only twice as low as the yield in a similar homogeneous aqueous solution and appears to be due to the consumption of part of the photochemically generated $Ru(bipy)_3^{2+}$ for the oxidation of organic components of the microemulsion.

The size of water droplets of the microemulsion is about 70Å, which is quite close to the size of the inner cavity of vesicles. This enabled us to use[19] the discussed results to create a reactive centre for the photocatalytic oxygen evolution in the inner volumes of the lipid vesicles, by introducing there $Ru(bipy)_3^{2+}$ and $[Co(NH_3)_4\ CO_3]^+$.

The sequence of reactions leading to O_2 production under illumination with visible light ($\lambda > 400$nm) seems to be the same for all microemulsions and the vesicle suspensions studied. An example of the conceptional sequence of these reactions for the vesicle system is given in Fig. 3. When passing from microemulsions to suspensions of vesicles, an approximately two-fold decrease in the yield of O_2 was observed, the most probable, reason for this being a weaker stability of the membrane to the oxidation by the $Ru(bipy)_3^{3+}$ complex in comparison with the organic phase of the microemulsion. The evolution of O_2 from the inner volumes of the vesicles is proved by the fact that a great excess of $EDTA^{2-}$ in the outer volume of vesicles had no effect on the yield of oxygen. Indeed, $EDTA^{2-}$ is known to reduce efficiently the $Ru(bipy)_3^{3+}$ particles, and introduction of $EDTA^{2-}$ into any available homogeneous system for photocatalytic O_2 evolution inevitably leads to the complete suppression of water oxidation.

Thus, the discussed experiments demonstrate a principal possibility to design the photochemical reaction centres for water oxidation to oxygen in the inner volumes of lipid vesicles even in the presence of the reduction medium (needed for hydrogen) evolution) in the outer volumes of vesicles and, therefore, to create on this basis a system with the whole cycle of water cleavage.

As has been mentioned above, for the creation of such system in the suspension of vesicles it is required that reaction (3) be conjugated with the process of electron transfer across the vesicle membranes. To accomplish this conjugation, we have attempted to modify system III (see Fig. 1) by introducing the catalyst of water oxidation $CoCl_2$ instead of $EDTA^{2-}$, into the inner volume of vesicles. Unfortunately, we have failed to observe O_2 evolution in such system. Neither inverting this system, that is, introducing $Fe(CN)_6^{3-}$ inside the vesicles and $Ru(bipy)_3^{2+}$ and $CoCl_2$ into the outer aqueous solution, leads to the production of O_2 in a measurable amount. Nevertheless, a set of catalytic oxidation processes assisted by $CoCl_2$ and conjugated with the electron phototransfer across the membrane was registered in the inverted system. This was evidenced by small amounts of CO_2 evolved from the inverted system under its illumination solely in the presence of both $CoCl_2$ and $Ru(bipy)_3^{2+}$. The results obtained allow one to conclude that the presence of lecithine membranes in aqueous solutions has an unfavourable effect on the activity and/or selectivity of $CoCl_2$-based catalysts for oxygen evolution. A possible reason for this phenomenon seems to be the adsorption of cobalt ions on the surface of the lipid membrane.

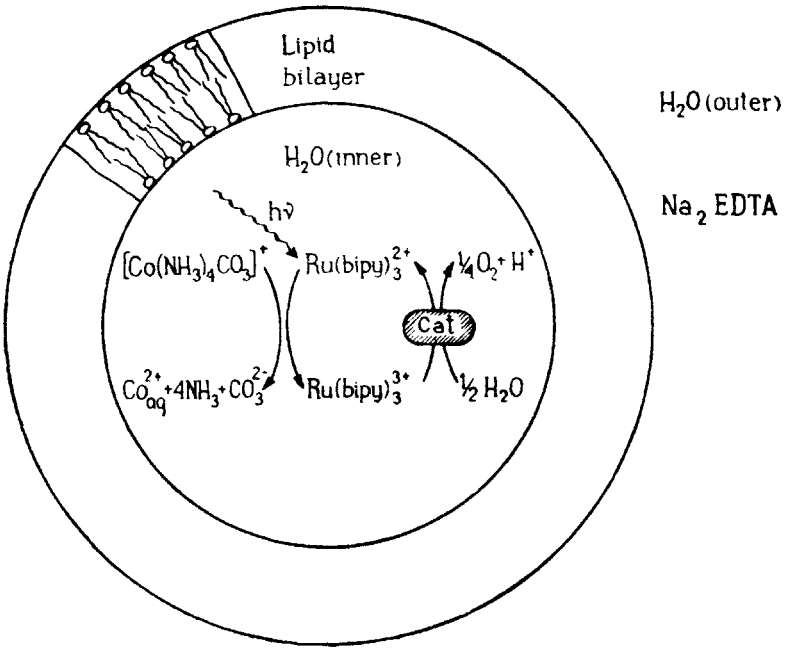


FIG 3 The photocatalytic reaction centre of oxygen evolution in the suspension of the lipid vesicles. Cat is the water oxidation catalyst based on cobalt compounds (*see the text*).

As has been shown previously, it is still possible to prepare the catalyst for water oxidation inside the vesicles when beginning from ammine complexes of cobalt(III). For this reason, we have attempted to conjugate the functioning of the reaction centre shown Fig. 3 with the electron phototransfer across the membrane. For this purpose, we have modified the system shown in Fig. 3 by introducing the electron carrier CV^{2+} into the vesicle membrane and a strong irreversible electron acceptor $NaIO_4$, instead of $EDTA^{2-}$, into the outer aqueous solution. Such modification resulted in the increase of the maximum total yield of O_2 obtained under illumination by more than a factor of 40 in comparison with the system without $NaIO_4$. Unfortunately, in spite of unambiguous evidences in favour of an extremely important role of CV^{2+} in the process under discussion, we cannot state with certainty that O_2 evolution in this system is caused by the electron phototransfer across the membrane onto IO_4^- but not by OI_4^- penetration into the inner volume of the vesicles. The study to answer this question is underway. At the same time, it was reliably established (by selective addition of $EDTA^{2-}$ to the inner or outer volume of the vesicles) that O_2 evolution, indeed, occurs in the inner volumes of the vesicles. Since four molecules of one-electron oxidant are needed to form one O_2 molecule, the number of $Ru(bipy)_3^{3+}$ oxidation-reduction cycles during the observed process of photo-stimulated O_2 evolution is *ca.* 4, even if one does not take into account the consumption of $Ru(bipy)_3^{3+}$ in side-processes of oxidation of organic compounds and the ligands of the complex-oxidant. Thus, one can conclude, that

in this case a real photocatalytic reactive centre of water oxidation to molecular oxygen was created in the inner volume of the vesicle.

Conclusions

From the above review it is seen that in recent years substantial progress has been achieved in the development of the molecular systems for solar energy conversion *via* photocatalytic water cleavage. Many catalysts have been developed for all the three steps of water decomposition under illumination : charge separation, hydrogen and oxygen evolution. The studies on the incorporation of catalysts of hydrogen and oxygen evolution into microheterogeneous systems based on lipid vesicles for the photocatalytic charge separation have allowed to create working (though up to date not conjugated with each other) photocatalytic reactive centres for both water reduction to hydrogen and its oxidation to oxygen. Therefore, the problems which we are facing now are to combine these centres in a single system in order to create the closed cyclic process of water cleavage. To do this we still need to look for more selective and active catalysts of oxygen evolution from water in the photocatalytic systems as well as to increase stability of the systems with respect to strong oxidants, generated in the step of photochemical charge separation. One may hope that once these problems have been solved, molecular photocatalytic systems, modelling natural photosynthesis, will present an applied interest for the solar energetics of the future.

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