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Vectorial phototransfer of electrons across lipid membranes

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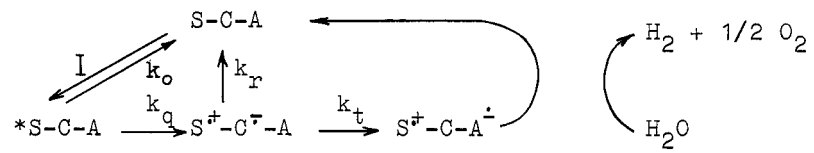
Abstract - Vectorial electron phototransfer across lipid membranes assisted by molecules - carriers of electrons can be used for providing spatially separated strong oxidant and reductant species. In this work the kinetics and mechanisms of the transmembrane vectorial electron phototransfer from donors located in the inner cavities of the lecithin lipid vesicles to acceptors located outside the vesicles were studied in two systems. The EDTA-ZnTPP-Methylviologen system contains tetraphenylporphyrinatozinc embedded into vesicular membrane. ZnTPP serves both as a photosensitizer and as a carrier of electron from EDTA to methylviologen. The $Ru(bipy)_3^{2+}$-Cetylviologen-$Fe(CN)_6^{3-}$ system contains an electron carrier - cetylviologen, embedded into the membrane. Under light the viologen transfers electron from photosensitizer - $Ru(bipy)_3^{2+}$ located in the inner cavity of the vesicle through membrane to $Fe(CN)_6^{3-}$ in the bulk volume. The possibilities are discussed of using photochemical systems based on lipid vesicles for accomplishing water cleavage.

INTRODUCTION

The past decade has been marked by the rapid progress in the photochemistry of structurally-organized molecular assemblies. Interest in this field is associated with its importance for photography, for the elucidation of photosynthesis mechanism and also for the development of chemical methods of solar energy conversion. For designing artificial systems that would permit light energy accumulation in the form of chemical fuels, this is the photodecomposition of water to dihydrogen and dioxygen that seems to be a most attractive process from both energetical and ecological points of view. The design of photochemical systems to perform this reaction is most often based on the following approach. The first step of this reaction involves the phototransfer of an electron either from a photosensitizer to an acceptor: $^*S + A \rightarrow S^+ + A^-$ or from a donor to a photosensitizer $^*S + D \rightarrow S^- + D^+$. The final stable products of water decomposition that are dihydrogen and dioxygen can be produced via subsequent catalytic processes of water reduction and oxidation by the particles A^-, S^- and S^+, D^+, respectively. Mechanistically this scheme is rather similar to the scheme of light energy accumulation during natural photosynthesis. But of course the difference between these two processes is that during the photosynthesis solar energy is accumulated as chemical energy of carbohydrates, whereas the photocatalytic decomposition of water produces energy as chemical energy of dihydrogen.

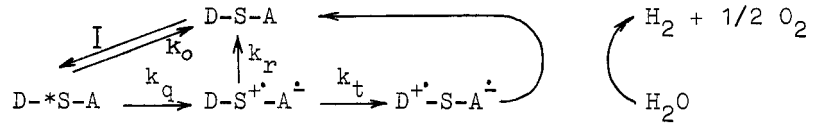
The major difficulty in the construction of photocatalytic systems for water decomposition is the necessity to inhibit the recombination reactions between S^+ and A^- or S^- and D^+ that are much faster than the complex catalytic reactions of water oxidation and reduction. That is why at present the possibilities to accomplish photocatalytic water decomposition at a sufficient efficiency in simple homogeneous systems seem to be rather vague. Inhibition of the recombination between oxidant and reductant in molecular photocatalytic system is likely to be realized by analogy with natural photosynthesis, i.e. via spatial separation of them in the system. It implies that system must contain spatially-organized molecular structures wherein S^+ and A^- or S^- and D^+ particles formed are spatially separated. Spacings that would ensure the suppression of these particles recombination must apparently be much larger than the sum of their radii. In this case the electron transfer, e.g. from $^*S$ to A, can be realized either via electron tunelling (ref. 1) or using an intermediate electron carrier (C) having a lower redox

potential than that of A. Photocatalytic water decomposition in the presence of such an electron carrier can be schematically represented, e.g as follows:



(I)

In steady-state conditions the rate of water decomposition W = a·b·I, where I is the intensity of light absorbed per unit volume of the system. The parameters $a = k_q/(k_q + k_o)$ and $b = k_t/(k_t + k_r)$ account for the probability of *S quenching by the electron carrier and of the spatial separation of charges, respectively. Note that the role of the electron carrier can also be performed by the particle S itself:



(II)

Thus in order to provide efficient generation of A^{-} and S^{+} (or D^{+}) and to inhibit their recombination one has to (i) construct molecular systems with the required spatial arrangement of the particles involved in charge transfer and (ii) provide large enough values of parameters a and b for these systems. Similarly to schemes I and II, one can construct systems that would be based on the primary electron phototransfer reactions:

$$*S\text{-}C\text{-}D \rightarrow S^{-}\text{-}C^{+}\text{-}D \quad \text{(III)} \quad \text{and} \quad D\text{-}*S\text{-}A \rightarrow D^{+}\text{-}S^{-}\text{-}A \quad \text{(IV)}.$$

Note also the evident similarity of the charge separation processes via schemes I-IV with that for natural photosynthesis.

One of the ways to realize schemes of type I and II is the synthesis of S-C--A or D-S-A triad molecules where fragments are connected with chains of covalent or coordination bonds. Here an essential progress has been achieved (ref. 2,3). It must be noted, however, that for further use of the separated charges, the above triads must be coupled with catalysts of water reduction and oxidation. So far no progress has been reported here. Another possible approach to the realization of schemes I and II consists in the use of self-organizing microheterogeneous systems such as microemulsions, micelles and vesicles. Vesicles are microscopic (d ≃ 300 Å) spherical particles formed by ca. 50 Å thick bilayer lipid (in what follows lecithin) membrane. Inside and outside vesicles there are immiscible water solutions of different composition. Membranes of these vesicles are formed by two monolayers of lecithin molecules whose polar "heads" contact with water phases and long hydrocarbon chains are directed towards the middle of the bilayer. If one performs the electron transfer across membrane with the help of an electron carrier (or a sensitizer) embedded into the membrane, it proves possible to obtain spatially separated products of electron phototransfer. Large enough ($1\text{-}10 m^2$ per 1 ml of suspension of vesicles) total surface area of the membranes makes it possible to acieve significant rates for this process. In this paper we present the results obtained in our laboratory in constructing such systems and in the investigation of the mechanism of their action.

RESULTS AND DISCUSSION

D-S-A system. This contains a water insoluble photosensitizer in vesicle membranes. Particles D and A are localized in water solutions on the opposite sides of the membrane. Systems of this structure have been examined most comprehensively. Chlorophyll (ref. 4,5), surfactant analogs of porphyrins (ref. 6,7) and of $Ru(bipy)_3^{2+}$ (ref. 8) and porphyrins (ref. 9-11) were used as photosensitizers.

In our systems tetraphenylporphyrinatozinc (ZnTPP) was embedded into the membrane. EDTA - an irreversible donor which cannot penetrate through the membrane was introduced into the inner cavity of the vesicle, while the bulk water phase outside the vesicle contained a reversible acceptor - methylviologen (MV^{2+}) that also cannot penetrate through the membrane (see scheme V below). Upon illumination of this system into ZnTPP absorption bands (λ = 510-650 nm), a vectorial electron transfer across the membrane takes place

with the effective quantum yield $\phi = 0.2\%$. The quantum yield of MV^+ accumulation in this system rises with increasing the temperature and the local concentration of ZnTPP in the membrane. At 297-333 K, i.e. both beneath and above the temperature of the gel-liquid crystal phase transition in the membrane, the accumulation rate of MV^+ is proportional to the square of the light intensity. It indicates that at least two light quanta are required to transfer one electron across the vesicular membrane. To determine the localization of excited ZnTPP molecules, we have examined the photoreduction of amphiphylic spin labelled molecules (derivatives of stearic acid containing the N-O· fragment inserted into the membrane)by ^{T}ZnTPP (see Fig. 1). It appears that the photoreduction rate for molecule having a spin label near the bilayer surface (at the fifth carbon atom counting from the carboxyl group) exceeds considerably that for the molecule with a spin label inserted into depth of the bilayer (at the sixteenth carbon atom).

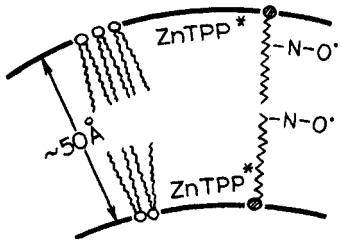
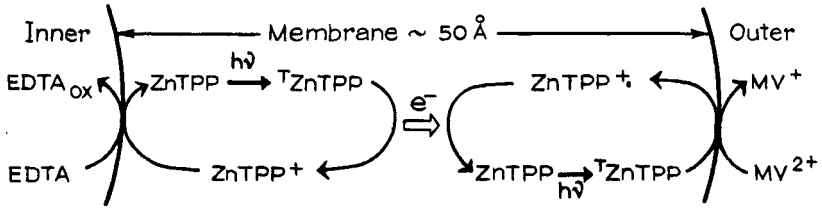


Fig. 1. Localization of ZnTPP and spin labelled molecules in vesicular membrane.

These results suggest that ZnTPP is localized mainly near the bilayer surface. Pulse photolysis experiments show that the primary photochemical reaction is electron transfer from ^{T}ZnTPP to MV^{2+}, and the intermediate particles taking part in electron transfer across the membrane are ^{T}ZnTPP and $ZnTPP^+$. The above data on the steady-state and pulse photolysis are qualitatively the same notwithstanding whether the illumination was performed into the B or Q band of the ZnTPP absorption. It seems to indicate that the decisive contribution to the transmembrane electron phototransfer is made by the triplet-excited ZnTPP molecules formed under irradiation into any of these absorption bands. The data obtained permitted us to suggest the following scheme for the transmembrane electron phototransfer (ref. 9,10):



(V)

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

$$^T\mathrm{ZnTPP}_{out} + MV^{2+} \xrightarrow{2\cdot10^{-5}\,s} \mathrm{ZnTPP}^{+\cdot}_{out} + MV^+$$

which is followed by the electron transfer across the membrane from the other excited ZnTPP molecule located near the inner surface of this membrane:

$$^T\mathrm{ZnTPP}_{in} + \mathrm{ZnTPP}^{+\cdot}_{out} \longrightarrow \mathrm{ZnTPP}^{+\cdot}_{in} + \mathrm{ZnTPP}_{out}. \qquad (1)$$

Finally the irreversible oxidation of EDTA takes place:

$$\mathrm{ZnTPP}^{+\cdot}_{in} + \mathrm{EDTA} \longrightarrow \mathrm{ZnTPP}_{in} + \mathrm{EDTA}_{ox}.$$

If this scheme is valid, one can expect that when both EDTA and MV^{2+} are located outside the vesicles the electron transfer from EDTA to MV^{2+} sensitized by ZnTPP can occur on the surface of the vesicle involving the participation of only one ZnTPP particle. In this case the rate of MV^+ accumulation must be proportional to the light intensity, and indeed it has been confirmed experimentally. The necessity for the participation of two triplet-excited porphyrin molecules in the transfer of one electron through the membrane, testifies to the fact that the transmembrane diffusion of the intermediate $ZnTPP^+$ cannot ensure electron transfer from one side of the membrane to the

other. Indeed, in case of the high transmembrane mobility of $ZnTPP^+$, the participation of the second excited porphyrin particle would not be necessary, as it really takes place when MV^{2+} is photoreduced in the presence of EDTA on the same side of the membrane. In the absence of $ZnTPP^+$ diffusion across the membrane reaction (1) can be provided by electron tunneling mechanism.

Taking into account that the rate-determining step of the transmembrane electron transfer is reaction (1), one can make an attempt to enhance the transfer using additional excitation of the ZnTPP molecules on the inner membrane surface. It could be done by virtue of energy transfer from some "antenna" collecting light and then transferring the excitation to the "reaction centers" (the ZnTPP molecules embedded into the membrane) similar to the action of a pull of the "antenna" chlorophyll in chloroplasts. In our experiments a water-soluble $Ru(bipy)_3^{2+}$ complex introduced into the inner cavity of vesicles was used as such "antenna". The lifetime of the triplet-excited state of this complex ($\simeq 0.6$ μs) is sufficiently high, so that before deactivation the excited complex can come into multiple collisions with the inner wall of the vesicle. It has been found that the introduction of $Ru(bipy)_3^{2+}$ leads to the sixfold increase of the transmembrane electron transfer rate. This effect is ascribed to, first, the spectral sensitization due to the light absorption by the complex in the spectral region where porphyrin does not absorb, and, second, to the two-three fold increase of ϕ (λ = 400-600 nm) apparently due to the energy (or electron) transfer from $Ru(bipy)_3^{2+}$ to $ZnTPP_{in}$.

S-C-A system. This is a further modification of the above system. This modification was based on, first, the above noted ability of $^*Ru(bipy)_3^{2+}$ to transfer energy or an electron to the molecules embedded into the membrane and, second, on the property of viologen free radicals to be extracted into an organic phase (ref. 12-13). A similar system has been examined by Shafirovich et al. (ref. 14). Their results in main features agree with our data (ref. 15-17). A photosensitizer, $Ru(bipy)_3^{2+}$, was put into the inner cavities of vesicles and a reversible hydrophobic electron carrier - cetylviologen (CV^{2+}) was embedded into membranes. In bulk solution outside vesicles an electron acceptor - $Fe(CN)_6^{3-}$ was located (Fig. 2). In the presence of EDTA

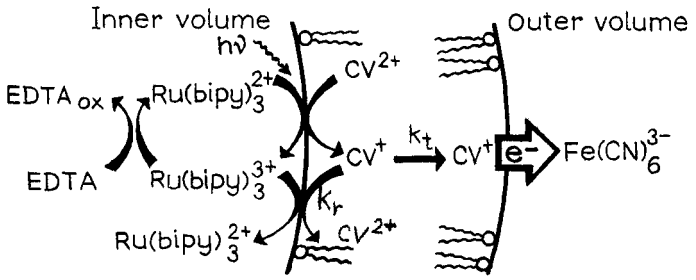


Fig. 2. Scheme for electron phototransfer across lipid membrane by the viologen radical in the $Ru(bipy)_3^{2+}$-CV^{2+}-$Fe(CN)_6^{3-}$ system.

in the inner vesicle cavity the illumination to the absorption band of $Ru(bipy)_3^{2+}$ leads to the transmembrane electron transfer from EDTA to $Fe(CN)_6^{3-}$ with ϕ_o = 15±5% (λ = 488 nm). The high quantum yield of the transmembrane electron transfer is obtained due to the efficient inhibition of the recombination between the primary products of electron phototransfer, i.e. $Ru(bipy)_3^{3+}$ and CV^+, because of the rapid reduction of $Ru(bipy)_3^{3+}$ by EDTA. In this case ϕ_o = a (see scheme I). In the absence of EDTA the recombination between $Ru(bipy)_3^{3+}$ and CV^+ becomes possible on the inner surface of vesicle. The conditions can easily be realized under which no more than one pair of $Ru(bipy)_3^{3+}$ and CV^+ particles are generated at a time nearly the inner surface of vesicular membrane. Note, that such conditions are fullfilled for solar light as a source of illumination. In this case the recombination is described by the first-order kinetics (ref. 18) with the rate constant $k_r = k_b/v$, where k_b is the bimolecular rate constant for the recombination of the same products in the inner cavity of the vesicle, v is the cavity volume. The quantum yield of the transmembrane electron transfer will be $\phi = \phi_o k_t / (k_t + k_r)$ (see scheme I).

We have measured k_t by the pulse photolysis and the stopped flow methods. In the latter case a suspension of vesicles containing CV^{2+} in their membranes and $K_3Fe(CN)_6$ in the inner cavities, was mixed with a solution of sodium dithionite. It led to the rapid reduction of about 70% of the total CV^{2+}

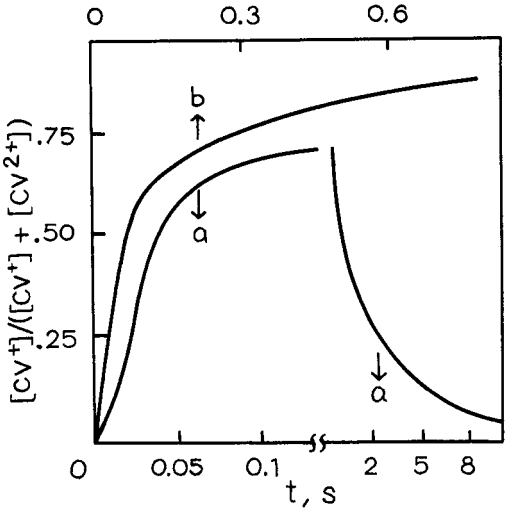


Fig. 3. Variations of CV^+ concentration in solution of vesicles that contain (a) and do not contain (b) 0.75 mol/l $K_3Fe(CN)_6$ in their inner cavities. Outside vesicles is the 0.01 mol/l sodium dithionite. The molar ratio viologen:lipid = 1:20.

amount in the sample, and then CV^+ reoxidation in its reaction with $Fe(CN)_6^{3-}$ was observed (curve a in Fig. 3). Rate constants of the first order with respect to CV^+ for these two reactions amount to 16 and 0.4 s^{-1}, respectively. They are independent of both the molar fraction of viologen in the membrane and the nature and concentration of the oxidizing agent placed into the inner volume. Assuming that the distribution of cetylviologen between the outer and inner membrane monolayers is uniform, the first step of the process can be ascribed to the reduction of CV^{2+} in the outer monolayer amounting to about 2/3 of the total membrane surface:

$$CV^{2+}_{out} \xrightarrow[Na_2S_2O_4]{k_1 = 16\ s^{-1}} CV^{+}_{out}. \qquad (2a)$$

Reoxidation of CV^+ is associated with its migration onto the inner surface of the membrane:

$$CV^{+}_{out} \xrightarrow{k_2 = 0.4\ s^{-1}} CV^{+}_{in} \quad (2b); \quad CV^{+}_{in} + Fe(CN)_6^{3-} \longrightarrow CV^{2+}_{in} + Fe(CN)_6^{4-} \quad (2c).$$

CV^{2+} ions cannot migrate through the membrane for the experimental time (<10 s). Hence as a result of reactions (2a)-(2c) the whole of cetylviologen is accumulated in the oxidized form near the inner boundary of the membrane. Vesicle destruction by a detergent makes all viologen molecules accessible for dithionite and leads to the reduction of the whole of viologen and ferricyanide. It is evident that during the transmembrane transfer of CV^+ ions there must arise an electric field in the membrane that retards the further transfer. The value of this field is proportional to the number of CV^+ ions transferred. But if besides CV^+ some other ions contained in the sample and capable of compensating the membrane charge are also transferred, starting from a certain instant, when the rates of CV^+ transfer and the charge compensation process become equal, the rate of CV^+ transfer will be determined by the rate of charge compensation process. It will be shown below that under the above experimental conditions (the initial number of CV^+ molecules is above 100 per vesicle), the rate constant k_2 = 0.4 s^{-1} actually corresponds to the process of ion transfer decreasing the membrane charge. These ions, perhaps, can be borate buffer components and also H^+ and OH^-.

It is essential that a decrease in the amount of $Fe(CN)_6^{3-}$ inside vesicles measured after the complete disappearance of CV^+ on the second segment of curve a, is more than twice as high as the CV^+ quantity formed during the first reaction step. It indicates that besides the CV^+ migration, there exists some additional channel for the electron transfer into vesicles. Data concerning this additional channel have been obtained in experiments similar to those described above, but in the absence of the electron acceptor in the vesicles inner cavities. In this case the addition of dithionite leads to the two-step reduction of cetylviologen with the rate constants 16 and 2.3 s^{-1} (curve b in Fig. 3).
During these steps approximately 70 and 30% of the overall amount of CV^{2+} in the membranes are reduced. Apparently, as before, the first step corresponds to the CV^{2+} reduction in the outer monolayer of the membrane, and the

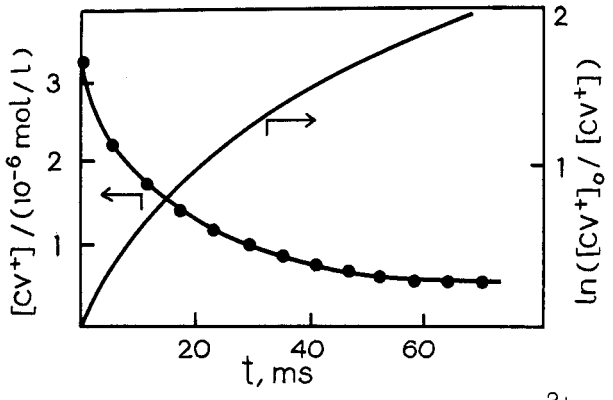


Fig. 4. Kinetics of CV^+ decay in suspension of vesicles containing 0.75 mol/l $K_3Fe(CN)_6$ in their inner cavities. The average initial content of CV^+ in the outer monolayer is 1.2 molecule per vesicle. Heavy line - experiment, points - calculation.

second accounts for the reduction of CV^{2+} from the inner monolayer. Taking into account that for $t < 10$ s CV^{2+} molecules do not migrate between the outer and inner monolayers, the slow step of the kinetic curve b (Fig. 3) can naturally be ascribed to the electron exchange:

$$CV^+_{out} + CV^{2+}_{in} \xrightarrow{k_3 = 2.3\ s^{-1}} CV^{2+}_{out} + CV^+_{in} \qquad (3)$$

taking place without a direct contact between the reacting particles, apparently, with the help of electron tunneling through the central hydrophobic area of the membrane. Reaction (3) is followed by the rapid reduction of CV^{2+}_{out} by dithionite. Assuming that electron transfer in reactions (1) and (3) is of the distant character, we mean that each of the reaction partners remains in its monolayer. The distance between the partners at a moment of electron transfer is equal to the sum of distances at which these partners can approach the interface between lipid monolayers. With this mechanism of distant transfer the constant k_3 as contrasted to k_1 and k_2 must be proportional to the rate of formation of $CV^{2+}_{in} + CV^+_{out}$ pairs with the favourable location of the partners, i.e. it must vary proportionally to the CV^{2+} concentration in the membrane. It has actually been confirmed in experiment.

The above statement about the retardation of electron transfer by the electric field induced in the membrane is based on the pulse photolysis experimental data. We generated CV^+ radicals in the outer monolayer of vesicle membranes, containing $Fe(CN)^{3-}_6$ in the inner cavities. If at the initial instant on the average less than one CV^+ radical per vesicle is present, the electron transfer is well described by the first-order kinetic equation. In case the initial concentration of CV^+ is higher than one molecule per vesicle at high reaction times the reaction is slowed down and its kinetics deviates from the first-order law (Fig. 4). This behaviour of the process can be described assuming that the electrons transfer into the vesicle with the initial number of cation radicals n takes place through the sequence of one electron transfer steps:

$$V_n(o) \xrightarrow{k_1} V_n(1) \xrightarrow{k_2} \ldots \xrightarrow{k_n} V_n(n) \qquad (4)$$

where $V_n(i)$ is the vesicle wherein the transfer of i electrons took place. The rate constants k_i can be calculated assuming that the transfer of CV^+ molecules induces an electric field in the membrane which increases the activation energy of transmembrane CV^+ transfer by a value $E = iF\Delta U/2$, where F is the Faraday constant and ΔU is the potential difference between the membrane surfaces formed during one CV^+ molecule transfer. The high rate for the lateral diffusion of ions over the membrane surface permits us to suggest that the membrane charge is uniformly distributed on its surface and to determine ΔU using the formula for a spherical capacitor. For these calculations the dielectric constant of the lipid phase was taken to be 2.1 with the inner and outer vesicle radii amounting to 85 and 125 Å, respectively. The kinetics of CV^+ decay was calculated according to the following scheme. The average initial number of CV^+ radicals per vesicle was determined from the experimental data, and then the concentrations of vesicles with different numbers n of CV^+ were found assuming that Poisson relationship is valid. Then using the kinetic equation for the sequence of reactions (4), the current concentration of CV^+ in vesicle with each n as well as the total concentration of CV^+ were calculated. Good agreement between calculation and experiment is seen from Fig. 4. When the transmembrane transfer involves more

TABLE 1. Rate constants for the transmembrane electron transfer (k_t) and for the recombination of viologen radicals R-N⊕-⊕N-R with $Ru(bipy)_3^{3+}$ in homogeneous solutions (k_h) and in suspensions of vesicles (k_r and k_b).

Substituent R	k_t / $10s^{-1}$	k_r / $10^2 s^{-1}$	k_b / (10^6 l/mol s)	k_h / (10^8 l/mol s)	$10^2 k_t/(k_t+k_r)$
Methyl	0.005	> 1000	> 500	17*	< 0.00005
Heptyl	11	46	22	15*	2.3
Cetyl	9	70	33	-	1.3
Benzyl	9	91	43	56*	0.98
Phenacyl	16	47	22	20*	3.3
2,4-Dinitrophenyl	12	28	13	38*	4.1
Phenyl	4	89	42	98**	0.45
4-Biphenyl	4.5	39	19	28**	1.1
4-Cyanophenyl	4	86	41	3.8**	0.46
4-Chlorophenyl	0.5	72	34	76**	0.07

* aqueous solutions; ** acetonitryl:ethanol = 2:1 solution

than eight CV^+ no deviation of the reaction kinetic from the first-order law is observed. Apparently, it corresponds to the case when the CV^+ transfer rate is determined by that of the charge compensation process. Rate constant for the transfer here amounts to 0.64 s^{-1} and is close to that measured by the stopped flow method (see above). The results indicate that to maintain the high rate of transmembrane electron transfer, it is necessary to ensure the compensation of the electric polarization of the membrane.

The rate constants for the transmembrane electron transfer by various viologens in the absence of an electric field have been measured and are listed in Table 1. It can be seen that the k_t value is strongly affected by the nature of substituent in the viologen molecule. For the best carriers the transfer time is below 10 ms.

Recombination between the primary products of the electron phototransfer in the inner vesicle cavities has been examined by the pulse photolysis method. Under experimental conditions the average number of $Ru(bipy)_3^{3+}$ and viologen radical pairs was less than one per vesicle. The rate constants k_r were measured and the corresponding bimolecular rate constants of recombination were calculated $k_b = k_r/v$ (see above). The k_b values were compared to k_h for reactions of the same substances in homogeneous solutions. It is seen from Table 1 that the rate constants of bimolecular recombination in lipid vesicles is considerably lower than those for homogeneous solutions. This stabilization of the primary products of charge separation can, apparently, be ascribed to the fact that viologen radicals are considerably more hydrophobic than dications (ref. 12,13). Hence viologen radicals immediately after formation (for less than 10^{-5} s) migrate deeper into the membrane. It hinders direct collisions between the radical and $Ru(bipy)_3^{3+}$ thus retarding their recombination. For the least hydrophobic methylviologen radical the recombination rate remains high. Note that here like in the reaction center of photosynthesis (RC) the primary stabilization of separated charges is obtained through increasing the distance between them. In RC it is achieved however, through electron transfer to the secondary acceptor, whereas in our case the primary acceptor itself changes its location for the more distant position from S^+.

CONCLUSIONS

The obtained values for the efficiency of spatial charge separation ($\simeq 10^{-2}$) suggest that the application of the carriers examined will make possible to construct photochemical systems wherein membrane separated charges are used in further reactions for water decomposition into O_2 and H_2. It has been noted above that for this purpose the appropriate catalysts must be introduced. The results so far obtained indicate the principal possibility to introduce catalysts for water decomposition into the required (either inner or outer) phase of vesicle suspension. Thus, for example, using hydrogenaze or fine-dispersed noble metals as catalysts, it appears possible to perform photochemical H_2 evolution either only in the inner vesicle cavities or in the bulk solution outside vesicles (ref. 19,20). It has also been reported (ref. 21,22) about photochemical water oxidation on the catalysts

(hydroxides-oxides of Co and Mn) immobilized on the outer surfaces of vesicle walls. The key problem now is the conjugation of vesicle systems for spatial charge separation with the catalysts selectively performing H_2 and O_2 evolution inside and outside vesicles. To do this one has in fact to construct peculiar molecular-sized photochemical microreactors on the basis of vesicles whose walls permit the vectorial electron transfer. The construction of such microreactors can be called molecular chemical engineering. One can expect that the principles for constructing of such systems tested in modeling photosynthesis, could be applied in future to realize other chemical reactions as well.

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