Russian Chemical Reviews **81** (12) 1146 – 1158 (2012) © 2012 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2012v081n12ABEH004277

Biomimetic utilization of solar energy

T S Dzhabiev, A E Shilov

Contents

I.	Introduction	1146
II.	Natural oxygenic synthesis	1148
III.	Modelling of the photosynthesis antenna	1151
IV.	Molecular devices of photoinduced separation and stabilization of opposite charges	1152
V.	Water reduction to hydrogen with one-electron reducing agents	1153
VI.	Many-electron oxidation of water by 'holes'	1154
VII.	Conclusions	1156

Abstract. The most interesting recent publications dealing with so-called artificial photosynthesis, *i.e.*, the development of photocatalytic converters of solar energy to the chemical bond energy using the fundamental principles of natural oxygenic photosynthesis, are discussed. The key stages of photosynthesis that should be reproduced in the artificial converters include light harvesting and transport of the light quantum to reaction centres where photoinduced charge separation occurs to give elementary reducing agents and oxidants (electrons and holes). The dark catalytic reactions involving the elementary reducing agents and oxidants give stable end products, namely, dioxygen and carbohydrates in the natural photosynthesis or dioxygen and hydrogen in the artificial photosynthesis. The bibliography includes 99 references.

I. Introduction

In the spring of 2011, Giulietto Chiesa, a well-known Italian political journalist and former member of European Parliament, stated that in five years a war for resources could start on the planet. He attributed this to an increase in world population, shrinking resources and other factors.† Meanwhile, some analysts believe that such a war has already started since the intention to control strategic hydrocarbon resources is at the core of many armed conflicts on the planet.[1,2]

T S Dzhabiev, A E Shilov Institute of Problems of Chemical Physics, Russian Academy of Sciences, prosp. Akad. Semenova 1, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax (7-496) 515 54 20, tel. (7-496) 522 18 94, e-mail: timur@cat.icp.ac.ru (T S Dzhabiev), tel. (7-496) 522 80 67, e-mail: shilov@icp.ac.ru (A E Shilov)

Received 29 September 2011
Uspekhi Khimii **81** (12) 1146 – 1158 (2012); translated by G A Kirakosyan

Academician V E Fortov is sure that 'in the modern world, only the countries with the well-developed fuel and energy complex capable of ensuring their energy independence and security may claim a place in the international arena'.[3] Therefore, many countries have adopted long-term programmes for search for new, mainly renewable, energy sources. Naturally, non-renewable sources, including nuclear power engineering, should also be developed. In the long run, there is no alternative to solar energy; therefore, of special interest are artificial converters of solar energy (SE) to electrical or potential energy of chemical bonds.

Nobel laureate Academician N N Semenov was the first to point out the necessity of development of renewable energy sources. He wrote: 'Rapid depletion of fossil fuels in future and the increase in the carbon dioxide content in the atmosphere confront mankind with the problem of creating a fundamentally new world energy strategy'.[4] Another Nobel laureate Academician Zh I Alferov stated that in 2100, 60% of electric energy will be generated by direct conversion of solar energy; nevertheless, today it is also necessary to develop biofuel production. It is worth noting that directors of American institutes focusing on solar energy J Mason, V Fthenakis and K Zweibel predict that solar power plants could supply 69% of the U.S.'s electricity by 2050. Most experts believe that energy of the future will be produced by solar and hydrogen power plants.[5–12]

Photosynthesis is the largest scale photoprocess on Earth. Unfortunately, only in a small fraction ($\sim$0.1%) of solar energy is captured by natural photosynthesis. In one hour of daylight, the Sun releases upon the Earth the amount of energy that is consumed by the entire population of the planet in one year. Therefore, solar energy can be considered an inexhaustible source as compared with other

† See http://news.rambler.ru/10074416/

conceivable sources, including fusion power, to say nothing of the fact that we still have to learn how to use it.

Products of photosynthesis are not only the energy basis of life, but also serve as a basis for the development of modern civilization — energy generation, industry, transport and other areas of human activity. Indeed, in all of these areas, the energy sources are the same products of photosynthesis in the form of fossil fuels stored in the bowels of the earth — coal, oil and natural gas. With the development of civilization, the fossil fuel depletion rate is ever increasing, and it is clear that, at current rates of consumption of fossil raw materials, they are not far from exhaustion. All this raises the problem of energy supply of mankind, and the need to address this problem becomes more apparent as time goes by.

A notable contribution to the solution to the energy problems of the future may be design of efficient photocatalytic converters of solar energy into the energy of chemical bonds. It seems that, even when the problem of controlled fusion is solved, the need for solar power will continue to exist, so that the question of conversion of solar energy will never lose its relevance. This fact had been emphasized by many scientists (Timiryazev, Vernadsky, *etc*.) long before mankind became really aware of limited fossil energy sources. The known Soviet physicist D S Rozhdestvenskii wrote in 1936: 'We blindly and stupidly look at how this precious energy flows past us on the ground, not making work... One might think that 10–20 years later the task of development of solar energy will rise specifically and compellingly, and probably, the second half of the 20th century will also be an era of photochemistry, as the second half of the 19th century was an era of electricity. But this new era in its scope will surpass many times the old one. Here the question is not only about a new form of energy, but also about that it will be gratuitous, like the air we breathe.'[13] It should be noted that the forecast for the exclusive role of photochemistry in the second half of the twentieth century was incorrect. In fact, the focus of the post-war years has been on nuclear power rather than on solar energy (Ref. 14, p, 375).

In 1961, the President of the Academy of Sciences of the USSR M V Keldysh at All-Union conference of scientists set the following problem for researchers: 'Science must achieve decisive progress in our knowledge of the mechanism of photosynthesis and in preparing for the implementation of artificial photosynthetic processes outside the plant'.[15]

Nowadays, interest in the utilization of solar energy has increased dramatically around the world. In many developed countries, there are national programmes for utilization of solar power with the appropriate funding for research in this area. Photosynthesis in plants is one of the most difficult problems of natural science, as noted by Academician A N Terenin in 1951 (Ref. 14, p. 361). The study of this problem requires the combined efforts of representatives of various scientific disciplines. It is clear that, for the successful design of an artificial solar power converter operating on the principles that lie at the heart of natural photosynthesis, it is necessary to identify the key stages of this complex physicochemical process. To solve this problem, from a variety of processes in photosynthesis, light phases have been selected that eventually lead to the dark oxidation of water and reduction of the primary acceptor of photosystem I (PS I); after that, an electron in the electron transport chain (ETC) can be used for the reduction of water to hydrogen rather than for the reduction of CO_2 to carbohydrates. To create a complete artificial system of photocatalytic splitting of water into the elements, it was decided to divide it into separate units that perform specific operations. Four such blocks were identified:[16]

1) device for the efficient collection of photons with different wavelengths and their delivery to the active reaction centre (RC) where opposite charges are photogenerated (the physicochemical photosynthetic antenna model);

2) photon-induced generation of strong one-electron oxidants and reductants, *i.e*., photoinduced separation and stabilization of opposite charges (electrons and holes);

3) catalytic oxidation of water by one-electron oxidants, a chemical model of the manganese cofactor (Mn-co) of the enzyme that oxidizes water in photosystem II (PS II) of oxygenic photosynthesis;

4) water reduction to hydrogen by one-electron reducing agents; such reactions can occur in some photosynthetic organisms when hydrogenase is added to chloroplasts.

Each of these blocks is a model of the appropriate stage of oxygenic photosynthesis. Figure 1 shows a simple scheme of oxygenic photosynthesis leading to the oxidation of two water molecules with formation an oxygen molecule and regeneration of the so-called biological 'currency' [*i.e*., with the formation of adenosine triphosphate (ATP) from adenosine diphosphate (ADP) and inorganic phosphate (Pi), and the conversion of nicotinamide adenine dinucleotide phosphate ($NADP^+$) to the reduced form NADPH *via* the addition of two electrons and one proton]. Electron transport chains in photosynthesis are shown in Fig. 1 by solid arrows and those in the proposed photocatalytic converters of light energy into chemical energy are shown by dashed arrows. For the formation of molecular products, photocatalytic systems that afford photochemical generation of one-electron reductants and oxidants in the so-called photocatalyst (PC) with their delivery through the ETC to efficient catalysts of non-complementary reactions are commonly used. These reactions are the oxidation of water to oxygen by one-electron oxidants (holes) and the two-electron reduction of protons of the medium by electrons. By the beginning of the 21st century, there have been created

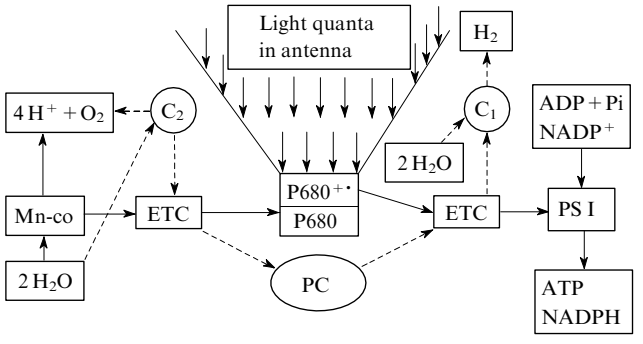


Figure 1. Scheme of oxygenic photosynthesis involving the water oxidation to oxygen, the reduction of $NADP^+$ to NADPH and transformation of ADP to ATP (solid arrows).
The dashed arrows show the paths of the photogenerated electrons and holes from the photocatalyst (PC) to the catalysts of formation of molecular products (C_2 and C_1).

photocatalytic generators of H_2, which are simple chemical models of bacterial (anoxygenic) photosynthesis and PS I of plant (oxygenic) photosynthesis. On the basis of dyes that absorb light in different regions of the solar radiation spectrum, artificial systems have been built in which excitation energy transfer is followed by electron transfer in the reaction centre analogue. These systems model a natural light collector ('antenna'), together with the RC of PS I. For efficient separation and stabilization of opposite charges, it has been proposed to carry out electron phototransfer in a strong field of the electric double layer (EDL), which under certain conditions can suppress the charge recombination. The possibility of efficient charge separation in an electric field has been confirmed in transfer reactions at the charged micelle–aqueous electrolyte or vesicle–electrolyte interface. It has been demonstrated that the separation of electron–hole pairs in a semiconductor (SC) is analogous to the separation of the oxidized donor and reduced acceptor in the electric field of the electric double layer. A hypothesis has been suggested that the transmembrane potential and the EDL potential gradient play an important role in the occurrence of natural redox processes. It has been shown that efficient water splitting into the elements cannot be achieved in homogeneous solutions. In general, there has been accumulated a significant amount of information to boldly move forward. Let us consider all the key photosynthesis stages, following the absorbed light quantum.

II. Natural oxygenic synthesis

1. Key stages

For utilization of solar power, a tempting possibility is to create an artificial chemical system that would split water into the elements using visible photons by the reaction

$$2\,H_2O = 2\,H_2 + O_2 - 572\ \text{kJ mol}^{-1}\ O_2$$

This reaction yields molecular hydrogen, a promising fuel and, in addition, environmentally friendly since the reverse reaction of hydrogen burning produces only water. Direct photolysis of water by visible photons is impossible since it does not absorb visible light; however, photosynthetic organisms can easily carry out the reaction of water splitting with the release of O_2; hydrogen is not released; rather, carbon dioxide is reduced to carbohydrates. The overall reaction of oxygenic photosynthesis is written as follows:

$$H_2O + CO_2 = (CH_2O) + O_2 - 469\ \text{kJ mol}^{-1}\ O_2$$

The energy of this reaction is not very different from the above reaction of water splitting into the elements. To create an efficient converter of light energy into the energy of chemical fuel on the basis of the water splitting into the elements, the principles of the natural photosynthesis can be used. In fact, the question is reduced to the construction of models of the key stages of photosynthesis on the basis of simpler chemical systems such that their concerted operation would lead to the desired process, *i.e.*, to 'artificial photosynthesis'.[16]

Studies of photosynthesis have been continued for 240 years. Their results have been described in many textbooks, monographs and reviews. According to geological data, 2.2 billion years ago, O_2 began to rapidly accumulate in the atmosphere. The appearance of oxygen-producing blue-green algae dramatically changed the course of evolution on Earth. Having the ability to use water for reducing CO_2, these algae have provided themselves with unlimited reserves of the electron donor. This was a result of the addition of PS II to PS I of green photosynthetic bacteria.

The current fossil fuels — coal, oil and natural gas — are a result of past photosynthesis, and the active process of their formation began about 300–350 million years ago.[17] Photosynthesis occurs in chloroplasts, subcellular entities 3–10 μm in size entirely penetrated by membrane structures, the main of which, grana, are stacks of thylakoids. Figure 2 shows the arrangement of the components of the photosynthetic apparatus in the thylakoid membrane of the chloroplast. Thylakoids, strongly flattened closed spaces

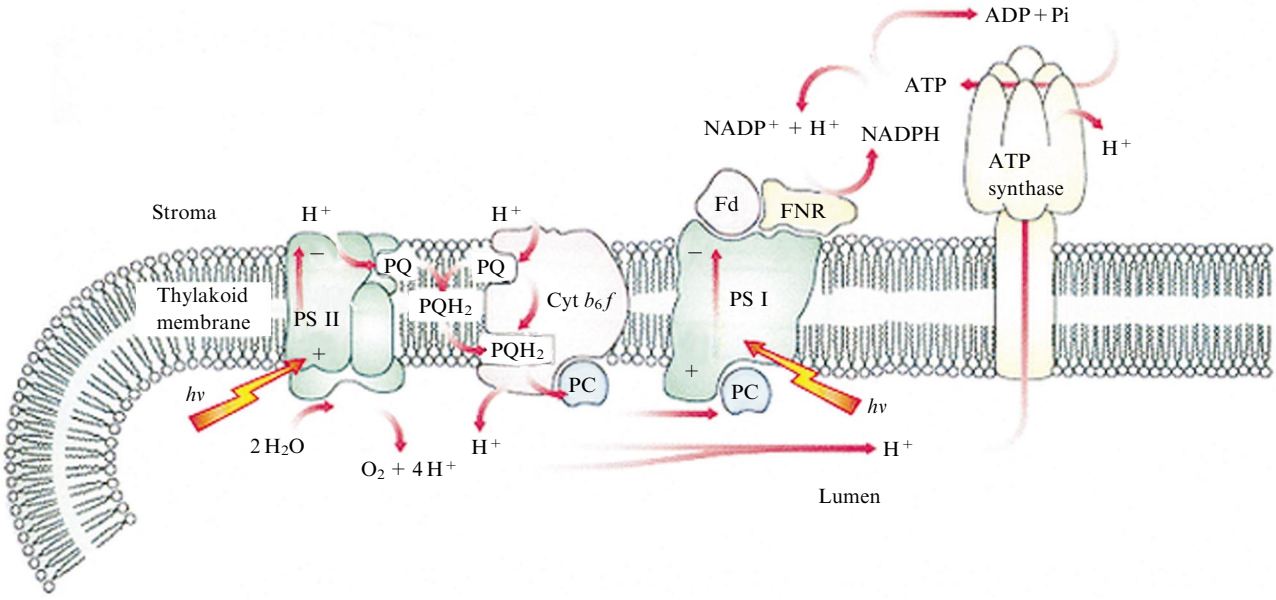


Figure 2. Arrangement of PS II and PS I with the ETC between them in the thylakoid membrane. PC is plastocyanin, PQ is plastoquinone, Cyt is cytochrome, and FNR is $NADP^+$ reductase.

resembling a coin, are composed of a double lipid membrane containing many different protein–lipid complexes. Almost all of the chlorophyll (Chl) is concentrated in grana; the cells of photosynthetic organisms contain rather large amounts of pigments, up to 5% of the dry weight or more. Chlorophyll, because of its special role in photosynthesis, is called 'the most important organic compound on Earth'.[18] The energy scheme of plant photosynthesis is shown in Fig. 3 as the conventional Z scheme. Chlorophyll is bound to protein globules to give pigment–protein–lipid complexes (PPLC) CP47 and CP43 in photosystem II and their analogues in photosystem I. Quanta of light absorbed by the pigments of the antenna eventually find themselves in the reaction centres of photosystems I and II, where charge separation processes and the subsequent electron-transfer redox reactions occur. Most of the chlorophyll in the photosynthetic unit (>99%) is involved in the collection of the scattered light quanta and their transport to the reaction centres.

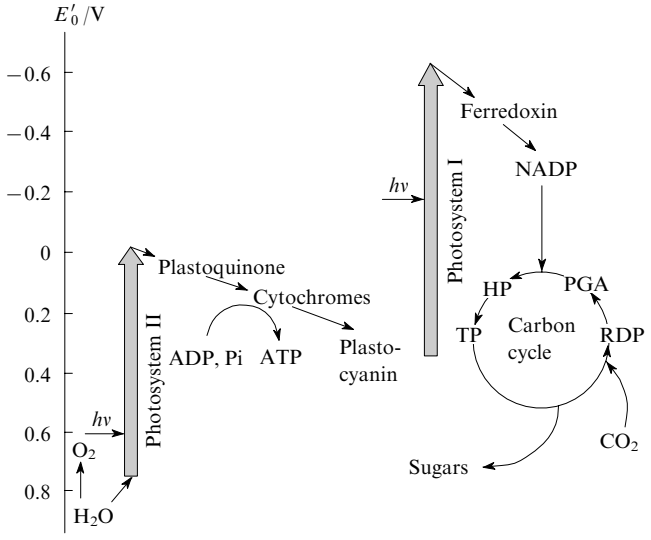


Figure 3. Energy Z scheme of oxygenic photosynthesis. RDP is ribulose diphosphate, PGA is phosphoglyceric acid, TP is triose phosphate, and HP is hexose phosphate.

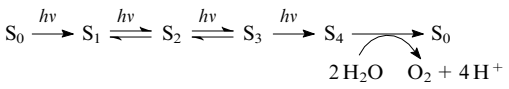
Once the excitation energy has been delivered to the reaction centre P700 (Chl dimer), electron transfer occurs to give radical cation $P700^{+\bullet}$. The electron that left P700 passes through the intermediate acceptor — chlorophyll Chl-695 — to ferredoxin (Fd).[19]

The primary electron donor in PS II is also a cluster of four chlorophyll molecules (P680) with two absorption maxima at 680 and 430 nm. The redox potential of the $P680^{+\bullet}$/P680 pair is sufficiently high (according to recent data,[20] it is 1.26 V) to oxidize water to oxygen. The electron lost by the excited P680 is transferred to pheophytin (Pp) with the redox potential ~ -610 mV; *i.e.*, the Pp radical anion is formed. This results in some dissipation of the excitation energy (see Fig. 3). Then, the electron passes through the ETC to $P700^{+\bullet}$ and returns it to its original state, losing some of its energy in the phosphorylation of ADP to ATP. The return of $P680^{+\bullet}$ to its original state is due to the water electron arriving to the $P680^{+\bullet}$ through the secondary donor in PS II.

The photon-induced generation of separated charges is a key process of solar energy utilization by photosynthetic organisms. Naturally, the composition and structure of the reaction centre are of great interest. The accumulation of four oxidizing equivalents in PS II is completed by the formation of the oxygen molecule and the release of four protons, which are involved in the creation of the transmembrane proton gradient (pH). The cofactor of the water-oxidizing enzyme in PS II contains four Mn ions and Ca^{2+} ion.

The possibility of the change in the oxidation state of the manganese cluster by several units has enabled the explanation of the known Kok model of S states. The Kok model has been proposed for the interpretation of experiments on oxygen evolution by chloroplasts exposed to a series of short saturating flashes of light.[21] Its essence lies in the fact that, after each flash of light, the oxygen-generating system goes to the next S_i state, and the sequence of flashes with a period of four leads to the initial state S_0 with the simultaneous release of an oxygen molecule from two water molecules (Scheme 1).

Scheme 1



Each intermediate S_i state is attributed to a definite oxidized form of the tetranuclear manganese complex involved in formation of molecular oxygen in the course of water oxidation. The assignment of specific oxidized forms of the manganese cluster in photosystem II of chloroplasts, as well as in model systems, to different S states has been addressed in many papers. There is no doubt that the release of the oxygen molecule requires the accumulation of four oxidizing equivalents. To do this, four electrons should be transferred through the ETC and at least four quanta of light should be spent, and taking into account that two photosystems are involved in electron transfer, each of which needs its own quantum, it takes at least eight photons to form one oxygen molecule. The experimentally observed dependence of the amount of released oxygen as a function of the number of short flashes shows oscillations with a period of four flashes. It is presumably impossible to unambiguously assign this dependence to successive stages of oxidation of the manganese cluster. These oscillations can be related to the complex oscillatory kinetics of the process, which is often observed in biological systems. Oxygen evolution in chloroplasts under light falls precisely into this category of processes, and this has been demonstrated under continuous illumination conditions.

Long study of plant photosynthesis has revealed the roles of nearly all components contained in chloroplasts in joint production of carbohydrates under the action of light. In many cases, not only the reactions of the components in the chloroplast are known but also quantitative data on the rates of the processes, such as the lifetime of the excited and ionic states, are available. All of these reactions familiar to chemistry occur, however, not in a homogeneous solution, but rather in a highly heterogeneous environment — at the interface of membranes of different composition with water or within very confined spaces, which impedes the use of some traditional methods of classical chemistry for analysis

of the object. This is the fundamental difference between homogeneous and microheterogeneous reaction conditions.

How are the components of the complex ETC arranged in the membrane structures of the chloroplast? Figure 2 shows the arrangement of the ETC components in the thylakoid membrane. It follows from this scheme that oxygen and the products of $NADP^+$ reduction are evolved on different sides of the membrane. Correspondingly, the oxidation and reduction centres in the photosynthetic unit are also spatially separated, which is a necessary condition for the efficient occurrence of the overall process. The aqueous phases on either side of the membrane contact with each other by means of special carriers located in the hydrophobic region of the bilayer lipid membrane (BLM) of the thylakoid. The electron transfer mechanism in chloroplasts of higher plants has been described by Blyumenfeld and co-workers.[22] The carrier is plastoquinone, which is readily soluble in the lipid phase of the membrane (like plastohydroquinone) and freely moves in it along the concentration gradient. The semiquinone radical anions are sorbed at the lipid–water interface and can freely move across the membrane only when they are converted to plastohydroquinone as a result of recombination and protonation.[22] After diffusion through the membrane, plastohydroquinone is oxidized by the reaction centre of PS I and again converts to plastoquinone, releasing two protons near $P700^{+\bullet}$. Then, plastoquinone moves to the other side of the thylakoid membrane to take a new pair of electrons and protons, thus connecting the membrane-separated aqueous phases. Simultaneous transport of electrons and protons by the plastohydroquinone shuttle results in generation of the pH gradient.[22]

2. Models of separate fragments of the photosynthetic apparatus

In the study of a complex process, such as natural photosynthesis, one needs to look for ways to simplify the object of study in order to understand the mechanism of action of individual units since their joint functioning constitutes the overall process. One efficient simplification of natural photosynthesis is the light-driven reduction of dyes, iron(III) compounds or other acceptors added to a chloroplast suspension, which was discovered by Hill in 1937 (the Hill reaction). In this case, the function of PS II is completely retained, and water is oxidized to release oxygen, while the action of PS I and subsequent dark reactions can be completely eliminated. The exogenic acceptors of the Hill reaction (for example, potassium ferricyanide) can be treated, to a zeroth approximation, as the model of the reduction portion of photosynthesis. Naturally, one should bear in mind that it is proposed to use a simple chemical substitute for the portion of the ETC of photosynthesis after one of the primary acceptor of PS II. Like ferricyanide, an inert anodically polarized electrode can function as the entire subsequent ETC if the photooxidative behaviour of adsorbed layers of chlorophyll is studied.

The efforts to further simplify PS II, namely, to carry out the Hill reaction in chlorophyll solutions, have been unsuccessful. However, Krasnovskii and Brin[23–25] have succeeded in achieving photostimulated oxygen evolution in water oxidation when inorganic photosensitizers — oxide semiconductors — were used instead of chlorophyll. Exposure to near-UV light of a suspension of tungsten trioxide in an iron sulfate solution or of zinc oxide in a ferricyanide solution is accompanied by the reduction of the salts to evolve oxygen. A similar reaction can be carried out on titania, even in the presence of the organic acceptor benzoquinone, however, with a much lower yield of oxygen (in this case, large amounts of CO_2 are formed).[26] The reactions studied by Krasnovskii *et al.* are referred to as inorganic models of the Hill reaction, although Korsunovskii[27] considered this name not to be quite accurate since part of the reaction (reduction of the acceptors) occurs also in the absence of the semiconductor. Many other inconsistencies between the proposed models and PS II may be pointed out.

Possible involvement of chlorophyll in redox transformations in the green leaves was suggested by Timiryazev, who confirmed this suggestion by performing reduction of chlorophyll by zinc metal. The reaction of reversible photoreduction of chlorophyll in a pyridine solution in the presence of ascorbic acid (the Krasnovskii reaction) was discovered in 1948. A logical continuation of this discovery was the creation of the models of PS I by Krasnovskii.[28] In aqueous solutions of surfactants, there can be observed the chlorophyll-photosensitized reduction of methylviologen and some dyes by ascorbic acid, cysteine or other electron donors. The methylviologen radical cation (MV^{2+}) is close in its reductive properties to the natural electron carrier ferredoxin in PS I, and these models mimic well the ability of P700 'to pump' electrons from the donor to the acceptor against the chemical potential gradient owing to the absorbed photon energy. For many biological processes (especially for large-scale natural oxygenic photosynthesis), an essential requirement is definite location of molecules and enzymes in the biomatrix. In this context, the interest of researchers in simple models of biomembranes not overloaded with various physiologically active substances, proteins, *etc.* is quite natural. A convenient simplified system for studying a wide range of surface biophysical phenomena is represented by black hydrocarbon films that are a chemical model of the BLM, the basic building block of cell membranes.[29] Artificial BLMs are distinguished from natural objects by the absence of the 'stuffing' of cell membranes and are widely used in research. There are many examples of the use of liposomes and vesicles, which are analogues of the thylakoid, to model both the spatial organization of the pigments in the photosynthetic apparatus and electron transfer across the membrane.[30]

Modelling of photosynthesis pursues both cognitive and practical goals. From the applied point of view, particularly attractive for biochemists is the possibility to produce hydrogen as a result of solar energy conversion by biocatalytic systems.[28,31–33] An interesting symbiotic system for generating hydrogen has been described that contains a plant (fern) and blue-green algae, which, in contrast to higher plants, has not lost the ability to fix molecular nitrogen from the atmosphere.[34] When the mixture is illuminated in the presence of a nitrogen source, the algae nitrogenase switches from the nitrogen reduction to the release of hydrogen from water. Usually, however, to change the route of the electron along the ETC in order to release hydrogen, hydrogenase — an enzyme that catalyzes the redox reaction of hydrogen — is specifically introduced into the chloroplasts or other smaller parts of the cell. Currently, attempts are made to extend the lifetime of such systems by stabilization of various components, immobilization of enzymes or replacement of unstable 'units' by more robust ones.

Bioconversion of light energy into chemical can be achieved using processes other than water splitting, for example, the reduction of nitrate to ammonium ion.[35] The reduction reaction is carried out by the same scheme as the above one for the reduction of protons of the medium, with the difference that the electrons from ferredoxin are transferred not to hydrogenase but to nitrate and nitrite reductases, which convert NO_3^- through NO_2^- to NH_4^+. For the implementation of this process, the 'natural' acceptors of the Hill reaction take up eight electrons from the ETC of chloroplasts.

The maximum efficiency of photosynthesis for the eight-quantum formation of the oxygen molecule is estimated at 15%–16%.[36,37] The observed values are considerably lower than the limiting one. In particular, the experimentally measured efficiency of solar energy conversion (based on the overall light flux) is as high as 6% for chlorella and even lower for other photosynthetics.[37] Unusually high values of the efficiency of photosynthesis occasionally reported in the literature (for example, 71%)[38] suggest that the authors forget that photosynthesis is a quantum process. In artificial molecular transducers, mobilization of one electron does not necessarily require spending two photons, as in chloroplasts; in addition, photophosphorylation of ADP, which also requires certain energy inputs, is unnecessary, *etc*.

III. Modelling of the photosynthesis antenna

A significant drawback of solar radiation from the point of view of practical use is its low density. Nature has bypassed this difficulty by creating a highly developed surface in the thylakoid membranes with a multiple increase in the number of light-harvesting pigments as compared with the concentration of the active centres. In addition, not only the photons that can be absorbed by chlorophyll but also harder photons (with a higher frequency) are used in chloroplasts. Such photons, while 'walking' over the pigments of the antenna, gradually lose part of their energy and have a frequency acceptable for P700 when they reach the reaction centre. Model systems can contain a set of photosensitizers absorbing light in different regions of the solar radiation spectrum. This type of integrated system of light harvesting has been realized by using a set of cyanine dyes that absorb photons of different frequencies and lead to the reduction of water to hydrogen.[39] The system with a set of dyes was more efficient than systems with individual photosensitizers, although the desired simple summation of the rates of the individual systems was not observed due to quenching of the triplet states of some dyes by other photosensitizers.

The interaction of several light-harvesting dyes with the imitator of the active site of PS I has also been studied in a micellar system.[39] When used together, two dyes (eosin and uranine) can lead to the nearly overall effect of the excitation energy transfer to the anthracene molecule acting as the model of the reaction centre in the chemical model of PS I. For collecting harder photons, a receptor that absorbs them should be selected. A good candidate for the role of the third photoreceptor in the spectral range of $\lambda = 450$ nm is the tris(bipyridyl)ruthenium complex. It was found that when eosin, uranine and $[Ru(bipy)_3]^{2+}$ are used as light collectors, the initial MV^{2+} reduction rate and, hence, the H_2 formation rate, in the presence of the Pt^0_{koll}/PVA catalyst (colloidal platinum stabilized by polyvinyl alcohol) is the sum of three separate rates.[39] The set of these three dyes can convert the photon energy in the range from 420 to 560 nm to the energy of chemical fuel (H_2). To implement a more favourable reaction route, water-soluble $[Ru(bipy)_3]^{2+}$ was replaced by a similar complex that has two long hydrocarbon 'tails' attached to one of the bipyridyl ligands (Fig. 4). This derivative exhibits surfactant properties and retains its photophysical properties; at the same time, its molecule is oriented optimally with respect to solubilized anthracene and efficiently transfers the excitation energy to the latter. In the case of the $[Ru(bipy)_2.(bipyR_2)]^{2+}$ derivative, the MV^{2+} reduction rate in photosensitized electron transfer from the irreversible donor EDTA (ethylenediaminetetraacetate) to MV^{2+} in a micellar medium made of surfactant Triton X-100 significantly increases (by more than an order of magnitude) as compared with the same photochemical system containing no anthracene, which indicates the participation of the latter in the electron transfer chain.

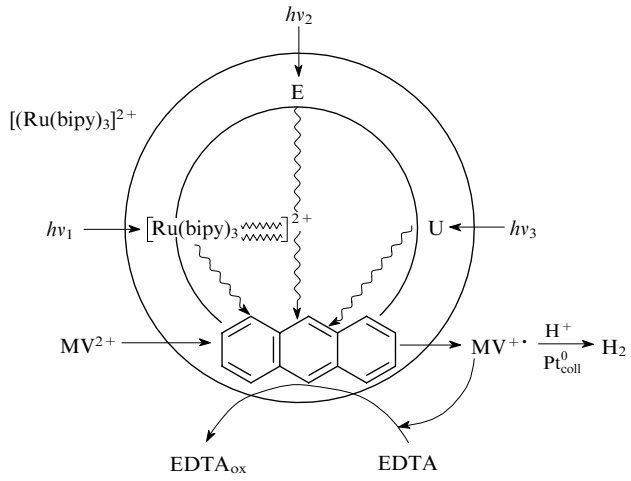


Figure 4. Schematic representation of a spherical Triton X-100 micelle (hydrophobic core and hydrophilic shell) and localizations of different dyes and reagents, including $[Ru(bipy)_2(bipyR_2)]$ ($R = n\text{-}C_{18}H_{37} =$ ∿∿∿).[39]
E is eosin, and U is uranine.

Thus, the efficiency of the photocatalytic H_2 generator can be enhanced by providing definite mutual arrangement of the system components. In addition, by varying the magnitude and sign of the charge at the interface between two different media, one can change the probability of radical ions leaving the radical ion pair and, thus, improve the efficiency of the overall process of the photoinduced charge transfer.

In photosynthetic systems of plants, one pair of chlorophyll molecules in the RC pigments is supplied by about 400 light-harvesting pigments.[40] The RCs of both types are equipped with their own antennas, which also contain extra pigments of the common light-harvesting system.

It is clear that the micellar models are not identical to the natural light-harvesting pigment–protein complexes; however, they model the main stages of natural systems: absorption in different regions of the spectrum and the energy transfer to anthracene, an RC analogue. The model

implies neither the singlet exciton energy transfer nor the interaction of two photosystems upon the redistribution of the absorbed light energy, but this is not necessary for the creation of artificial chemical systems converting solar energy into chemical energy. After all, we have to use the principles of natural photosynthesis, but not to copy it.

An appropriate choice of the model antenna components for the combined action of several photosensitizing dyes makes it possible to rule out the loss in efficiency of the system as a whole as compared to the algebraic sum of the efficiencies of 'monochromatic' subsystems. It is worth noting that a wider variety of dyes can be used in chemical models as compared with the natural process where chlorophyll mainly performs a multitude of functions. Indeed, it serves as a light collector in the antenna, as a kind of retranslator in excitation energy transfer and as a redox agent in the RC. In model systems, a more suitable reagent can be used as the RC (in our case, anthracene, which is quite unsuitable as a photosensitizer). Conversely, for photon absorption and transfer, dyes with favourable photophysical properties (eosin, uranine) but poor redox parameters for electron transfer to the intermediate acceptor or to the catalyst of molecular hydrogen generation can be used in model systems.

The use of the energy transfer principle (mainly, by the triplet–triplet mechanism, but the other possible mechanisms, namely, singlet–singlet or singlet–triplet, are not ruled out) affords the near-unity quantum yield of $MV^{+\cdot}$ in light-driven reduction of methylviologen by various irreversible electron donors. Nowadays, a lot of attention is paid to the fullest possible coverage of the solar radiation spectrum by different photoreceptors.[41–54] Most studies focus on visible light sensitization of semiconductor solar cells. Considerable progress in this area has been achieved by Grätzel and co-workers,[55] who synthesized a compound based on Zn porphyrin absorbing light over almost the entire visible spectrum. This is one of the greatest achievements in modelling antennas of photosynthetic organisms.

IV. Molecular devices of photoinduced separation and stabilization of opposite charges

For water splitting, it is necessary that strong one-electron reductants and oxidants should manage to generate, respectively, H_2 and O_2 on catalysts before recombination. It is hard to imagine a successful competition of many-electron processes of O_2 and H_2 generation with recombination reactions of strong one-electron oxidants and reductants. The question arises why numerous attempts to split water into the elements in a homogeneous solution have failed? This question is very important, and we will dwell on it in more detail.

Let us consider a homogeneous system in which the following redox reaction occurs:

$$Ox + n\,e \rightleftharpoons Red$$

The lower the activity of electrons in solution, the higher the oxidation potential of the system.[56] Conversely, the higher the chemical potential of electron activity in solution, the higher the reductive capacity of the solution. Whence follows that the requirements for a solution in which the oxidation and reduction of the substrate should occur simultaneously are contradictory. On the one hand, a strong oxidative medium is mandatory for achieving the high substrate oxidation rate; on the other hand, the high reductive capacity of the solution is required for the reduction to be smooth. Thus, under homogeneous conditions, one can hardly count on creating an efficient chemical system for solar-to-chemical energy conversion.

What are possible ways to overcome these difficulties, in particular, how to avoid the recombination of opposite charges formed in the primary photocatalytic event? It seems like that the rapid recombination of charges can be suppressed by means of electric fields that emerge at the interface. Indeed, according to the Gui–Chapman electric double layer theory,[57] a considerable gradient of the potential emerges in the contact area of two phases if there exist fixed charges or dipoles (Fig. 5*a*). The electric field strength in aqueous solutions is as high as 10^5–10^6 V cm^{-1} (Ref. 57). This is quite sufficient to prevent the recombination of two oppositely charged ions in the EDL. As is known, such strong fields lead to dissociation of the Chl^+ and Chl^- ion pairs formed upon light-driven electron transfer in the chlorophyll dimer.[58] An analogous phenomenon of generation of current carriers upon the photoexcitation of charge-transfer complexes in electric fields of $\sim 10^4$ V cm^{-1} was observed in photoconductive polymers doped with tetracyanobenzene.[59]

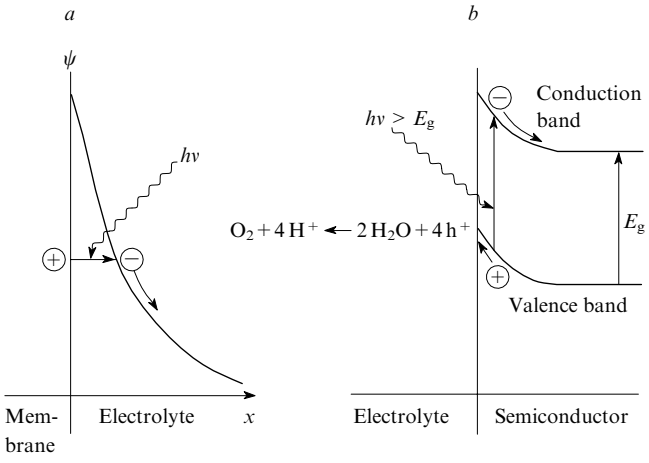


Figure 5. Electrostatic potential (ψ) at the interface (*a*) and band bend in the near-surface region at the semiconductor–electrolyte interface (*b*).[60]
h^+ is 'hole'.

The energy diagram of the SC electrode contacting with the electrolyte (Fig. 5*b*) shows that, in the near-surface layer of the SC, the bands are bent; this bend reflects the region depleted in major carriers. As a rule, this region of the change in the level ranges from 50 to 2000 Å deep into the SC. The absorption of a light quantum with $h\nu > E_g$ (E_g is the band gap) leads to the appearance of an electron in the conduction band and of a hole in the valence band. The recombination of this electron–hole pair is prevented by the strong electric field in the near-surface layer of the SC electrode. The electrons driven by this field move deep into the SC, while the holes tend to diffuse to the interface. This is the charge separation mechanism in an n-type semiconductor. The similarity of the charge separation mecha-

nisms in these cases is evident. Although the material of the membrane in Fig. 5 *a* should in no case have semiconducting properties, the physics of the phenomenon is the same in both cases: a strong electric field prevents the recombination of opposite charges (ion pairs or electron–hole pairs).[60]

A design can be proposed for model systems that would only separate the two half-reactions in space, but also prevent the fast recombination of ion pairs generated in the primary chemical event. If a molecule of a sensitizer (for example, chlorophyll) is fixed in the membrane by means of a long hydrocarbon 'tail' so that the chromophore is located at the interface (Fig. 6), then for the negatively charged membrane surface after electron transfer to the acceptor molecule, the reverse process will be slowed down by the electric field. The oxidized sensitizer should be reduced by an electron that arrives from the other side of the membrane. Electron transfer through the phospholipid membrane can be realized by means of quinones. Quinone on the left side of the membrane is reduced to hydroquinone, passes through the membrane and is again oxidized to quinone on the right side, thereby losing electrons to the sensitizer and protons, to the medium. Such a mechanism of electron transfer through the membrane in the chloroplasts of higher plants has been proposed by Blyumenfeld and coworkers.[22]

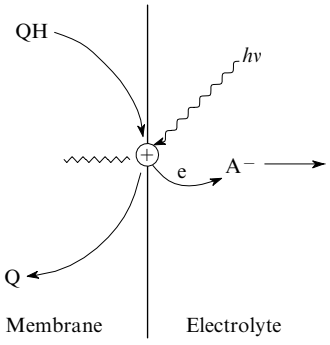


Figure 6. Separation of opposite charges in the electric field of the electric double layer.[60]

Naturally, different options of a specific device are possible, but the basic principle of charge separation by the electric field must be the same. Because of the wide distribution of membrane structures in plant chloroplasts, it is tempting to advance the hypothesis of the crucial importance of the electric fields at interfaces to the mechanism of stabilization of the photogenerated charges in natural photosynthesis. The role of these fields has been emphasized by many researchers. In particular, in a review article on the energy conversion in the functional membrane of photosynthesis, Witt [61] wrote that the electric field ran all through the energetics of photosynthesis.

It should be noted that most studies addressing the effect of the electric field on the different processes in photosynthesis have focused on the transmembrane potential gradient, although sometimes the fields at the interface (EDL) have also been considered.

Thus, the inclusion of different cross reactions of one-electron oxidants and reductants compels us to conclude that the complete water splitting reaction in a homogeneous system with a noticeable performance is impossible. It should also be noted that most of the catalysts of both half-reactions are colloids or suspensions, obeying electrochemical laws ('microelectrodes'). The performance of a microelectrode depends significantly on the oxidation potential of the solution, and creating favourable conditions for the operation of one of the catalysts will inevitably worsen the conditions for the operation of the other one. For the photodecomposition of water to occur at a noticeable rate, the system requires a special design that prevents fast reverse transfer of the photomobilized electron to the original 'parent' donor.

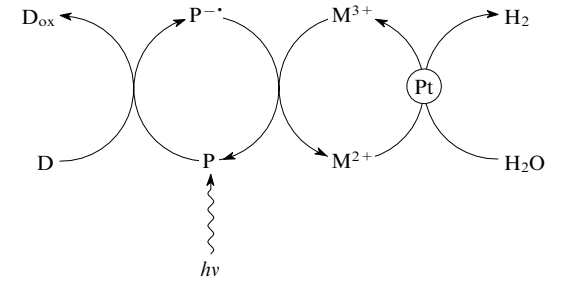
In photosynthesis, the oxidation of water to O_2 occurs on the inner side of the thylakoid membrane, while relatively stable intermediate reductants form on the outer side; thus, the oxidation and reduction reactions are spatially separated. It is clear that, in model systems as well, the two half-reactions of the photoinduced water splitting should be carried out in different places, for example, in different cells of a photoelectrochemical converter or on different sides of a photocatalytic particle in semiconductor suspensions.[62] Therefore, considerable recent interest has been shown in photochemical reactions occurring at the interface — in micelles, microemulsions, vesicles, liposomes and other organized structures. The most appropriate models of the thylakoid membrane of chloroplasts are liposomes and vesicles,[63] and the most easy-to-use models are microemulsions and micelles.[64]

The problems of charge separation in biological systems have received much attention, which is, unfortunately, not the case for chemical systems. Charge separation processes are mainly studied in complex molecules containing electron donors and acceptors at different distances from each other,[65,66] although this is not exactly what happens in real biological systems. In our early works, we studied the strong effect of the charge on the surface of the micelles or vesicles on the rate constants for electron transfer from a donor to an acceptor, as well as for electron transfer through the bilayer lipid membrane in vesicles and liposomes.[16,39] However, these studies are insufficient to clarify the most important stage of natural and artificial photosynthesis — photoinduced separation of opposite charges. All currently available practical devices for light energy accumulation use SC materials to prevent recombination of photogenerated charges. As for molecular systems, this problem is far from being solved. It is necessary to significantly intensify studies, remembering that nature managed to create a highly efficient design capable of separating opposite charges with a near-unity quantum yield, which still cannot be achieved with any semiconductor.

V. Water reduction to hydrogen with one-electron reducing agents

Reactions of water reduction by one-electron reducing agents have been well documented. Many years ago, we studied the reduction of protons of the medium to hydrogen catalyzed by colloidal 'microanodes', as well as the first purely chemical models of PS I and bacterial (anoxygenic) photosynthesis,[16,39] and after reaching almost limiting activities of the formation of the target products in both the dark and photoinduced systems, switched to the simu-

lation of other stages of photosynthesis. Krasnovskii *et al.*[67] described a similar model of PS I a little bit earlier than us, but they used hydrogenase as the catalyst for the generation of molecular hydrogen; therefore, our systems free of enzymes have been recognized as the first purely chemical models of bacterial photosynthesis and PS I. Photocatalytic systems leading to the formation of hydrogen in the photoinduced oxidation of irreversible electron donors are described by a simple cyclic pattern (Fig. 7). This Figure shows the photosensitizer dyes (P), electron donors (D), mediators (M) and catalyst (Pt) of hydrogen molecule generation that we studied. Similar systems for hydrogen generation are still actively studied.



D	P	M
EDTA	Acridine Yellow	Salicylides
Cysteine	Trypaflavine	V^{3+} and Eu^{3+}
Triethanolamine		MV^{2+}
H_2S		

Figure 7. Schematic representation of simple chemical models of PS I and bacterial (anoxygenic) photosynthesis.[16]

Microalgae capable of fixing nitrogen, such *Chlamidomonas reinhardtii*, in the presence of hydrogenase can spend some of their one-electron reducing agents for generation of hydrogen.[68] Similar unicellular green alga *Chlorella*, together with iron hydrogenase, also generates hydrogen,[69, 70] and its yield increases in the absence of sulfur as an endogenous substrate.[71, 72] Such studies are a continuation of the investigation by Gaffron, who discovered in 1942 the metabolic evolution of hydrogen instead of oxygen by oxygenic photosynthetics under anaerobic conditions. Experts believe that photohydrogen obtained using unicellular algae will be able to compete with other methods of its production, if the efficiency of photobiological systems is increased above 10%.

Although the models of PS I still use colloidal platinum as a catalyst as was done in our first purely chemical model,[16] there are new catalysts for hydrogen molecule generation — mono- and binuclear Pt^{II} complexes[73] and Ir^{III} and Rh^{III} complexes;[74] in the presence of the latter, the turnover number of the active site of 5000 has been observed at the quantum yield of hydrogen > 34%. Bis(dimethylglyoximato)cobalt[75] and a cobaloxime supramolecule[76] can also be used. Quite recently,[77] a system has been described in which an electron is transported photochemically from ascorbate entrapped in the inner waterpool of vesicles to MV^{2+} dissolved in the outer aqueous solution and relayed to a Pt(II) complex with a long organic 'tail'. Thus, study of the chemical models of PS I is actively continued, although no fundamental ambiguities are left, and model systems are gradually improved and optimized. It can be argued that the catalytic water reduction unit for generating hydrogen has been completely designed.

In addition to molecular models of PS I, SC models are also actively developed. For example, it has been shown[78] that Ni^0 nanoparticles photodeposited on the SC surface ($Cd_xZn_{1-x}S$ nanostructures) efficiently catalyze the evolution of hydrogen from water–alcohol mixtures and aqueous solutions of sodium sulfite. Since there are currently no problems with the catalysts for molecular hydrogen generation, most studies focus on the search for organic sensitizers that enable the use of visible solar radiation.

VI. Many-electron oxidation of water by 'holes'

The second pure dark reaction of photosynthesis is the many-electron oxidation of water by holes. It is considered the most important and difficult to study. Some researchers consider the transition of natural photosynthesis to water as the source of electrons for the reduction of carbon dioxide as a revolution in the development of photosynthetic organisms (a kind of 'big bang' in the evolution of photosynthesis). There is no doubt that the transition of chemotrophic photosynthetics from exhaustible organic and inorganic electron donors for the construction of their structure to water, an unlimited source of hydrogen, about 2.7 billion years ago is an outstanding event. However, the earlier creation of the system of photoinduced charge separation in the form of PS I was even more important.

Long before the moment when nature needed to use water as an electron donor in photosynthesis (about 3 billion years ago), a photosystem effectively functioned that reduced carbon dioxide to carbohydrates, using the energy of visible photons and sulfide or other electron donors. In the transition to water as a source of electrons, nature had to invent a special device that enabled the noncomplementary four-electron oxidation of two water molecules to an oxygen molecule by one-electron oxidants ($P680^{+\bullet}$ holes in PS II). In this process, Mn-co in PS II acts as the catalyst of non-complementary reaction of water oxidation to oxygen.

In oxygenic photosynthesis, the manganese cofactor Mn-co of the water: plastoquinone oxidoreductase enzyme, which functions in PS II, is oxidized stepwise by four one-electron $P680^{+\bullet}$ oxidants. Once Mn-co has accumulated four holes, it oxidizes two water molecules to a dioxygen molecule and returns in the initial state. The oxidation of water in PS II can be described by the equation

$$4\,P680^{+\bullet} + 2\,H_2O \longrightarrow 4\,P680 + O_2 + 4\,H^+$$

Nowadays, most researchers agree with such a reaction of concerted formation of an oxygen molecule in photosynthesis (see, *e.g.*, Refs 79–82). However, in the recent past, such an agreement has not been observed, and the oxidation of water has been intensively studied by different methods. We have also tried to understand the mechanism of action of Mn-co, exploring a simple functional chemical model Mn-co–sulfuric acid solutions of Mn^{IV} sulfate. When this chemical model is exposed to light or heated, Mn^{IV} compounds are reduced to oxidize water. At low oxidant concentrations ($[Mn^{IV}] < 1$ mmol litre^{-1}) and rather high temperatures of the reaction mixture (85–100 °C), the oxidation of water to an oxygen molecule occurs in the

coordination sphere of binuclear manganese complexes Mn_2^{IV}, which constitute the dissolved oxidant.[83] In the elementary step, the binuclear complex Mn_2^{IV} was reduced by coordinated water to Mn_2^{II}, which reacted with Mn_2^{IV} to give Mn_2^{III}. According to the scheme of the process, the initial reaction rate increased linearly with increasing concentration of the oxidant, while the kinetic curve of oxidant consumption in a separate experiment did not obey the law of monomolecular reaction.[83] To explain the observed trends, the set of all binuclear manganese complexes existing in the reaction mixture, *i.e.*, $Mn^{IV}Mn^{IV}$, $Mn^{IV}Mn^{III}$ and $Mn^{III}Mn^{III}$, should be considered. Only the first dimer is active since it has the necessary number of holes ($4\,h^+$) to oxidize two water molecules to one oxygen molecule. The other two clusters are unable to oxidize water since they have no the necessary number of holes to generate oxygen while the oxidation of water to other products ($HO^{\bullet}$, H_2O_2 and $HO_2^{\bullet}$) is thermodynamically unfavourable (Fig. 8).[84] It

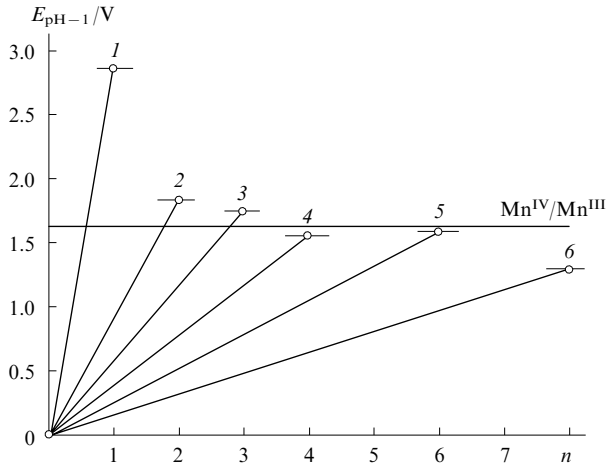


Figure 8. Standard potential of water oxidation *vs.* the number of transferred electrons (n).[84]
(*1*) $HO^{\bullet}$ (H_2O-e-H^+), (*2*) H_2O_2 ($2\,H_2O-2\,e-2\,H^+$), (*3*) $HO_2^{\bullet}$ ($2\,H_2O-3\,e-3\,H^+$), (*4*) $^1O_2$ ($2\,H_2O-4\,e-4\,H^+$), (*5*) O_3 ($3\,H_2O-6\,e-6\,H^+$), (*6*) O_4 ($4\,H_2O-8\,e-8\,H^+$).

follows from the figure that the redox pair Mn^{IV}/Mn^{III} is capable of four-electron oxidation of two water molecules to oxygen, six-electron oxidation of three water molecules to ozone, eight-electron oxidation of four water molecules to oxozone, *etc*. Naturally, these many-electron processes can occur only in the coordination spheres of clusters capable of coordinating the corresponding number of water molecules. Binuclear manganese complexes Mn^nMn^m are related by the redox equilibrium

$$Mn^{IV}Mn^{IV} + Mn^{III}Mn^{III} \rightleftharpoons 2\,Mn^{IV}Mn^{III}$$

The equilibrium constant of this reaction (K) determines the oxidant consumption kinetics. If $K = 0$ (the lack of negative feedback [85]), the consumption kinetics of the Mn^{IV} oxidant obeys an exponential law shown by curve *1* on the phase plane [86] in the coordinates 'dimensionless rate (w/w_0) – conversion $(1-x)$', where $x = [Mn^{IV}]/([Mn^{IV}] + [Mn^{III}])$ is the mole fraction of the Mn^{IV} oxidant in the $Mn^{IV}-Mn^{III}$ mixture (Fig. 9). In the other limiting case

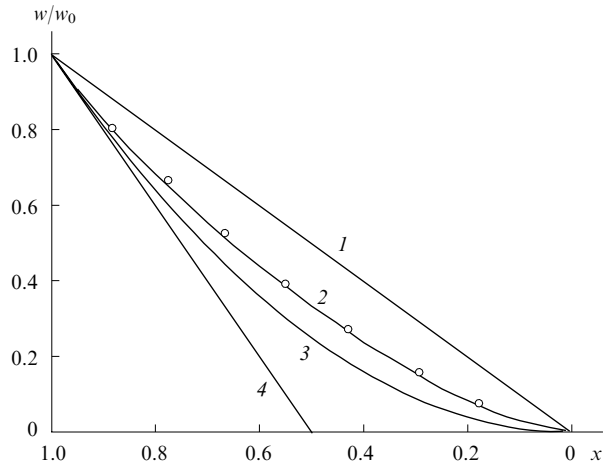


Figure 9. Phase trajectories of intracluster processes in dimers at different equilibrium constants (K) between the $Mn^{IV}Mn^{IV}$ and $Mn^{III}Mn^{III}$ complexes (see text).[84]
Lines are calculation, data points are experiment.

when $K \to \infty$ (very strong negative feedback), the kinetics of Mn^{IV} autooxidation with water is also exponential (curve *4* in Fig. 9), however, the process stops after one half of the oxidant has been reduced (at $x \geqslant 0.5$ $w = 0$). At $K = 4$, the phase trajectory of the Mn^{IV} consumption is described by curve *3* in Fig. 9. The same curve represents the phase trajectory of any bimolecular reaction

$$A + A \longrightarrow \text{products}$$

At low oxidant concentrations and high temperatures, the process is described by phase trajectory *2*, calculated for $K = 1$ (the points in phase trajectory *2* have been obtained from experimental data). The equality $K = 1$ means that the redox potentials of the $Mn^{IV}Mn^{IV}/Mn^{IV}Mn^{III}$ and $Mn^{IV}Mn^{III}/Mn^{III}Mn^{III}$ pairs are the same. The fact that only one O_2 molecule is actually released in this step is confirmed by the phase trajectory constructed on the basis of the O_2 formation kinetics. It demonstrates that the stoichiometric coefficient for the oxygen molecule generated in the course of the intracluster concerted oxidation of two coordinated water molecules is unity.

At oxidant concentrations $[Mn^{IV}] \geqslant 3$ mmol litre^{-1}, the initial oxidant consumption rates have proved that a second channel was added to the known process of reduction of the Mn_2^{IV} complex; the rate of the second process was proportional to the squared oxidant concentration: $w_0 \sim [Mn^{IV}]^2$. Such a behaviour is due to the fact that, with increasing oxidant concentration, some of the binuclear complexes Mn_2^{IV} are dimerized to give tetranuclear Mn_4^{IV} clusters; the rate of water oxidation by these clusters exceeds by more than an order of magnitude the corresponding k_0 in the case of Mn_2^{IV}. Thus, the stoichiometric coefficients of the oxidant and reaction products in the equation describing the elementary intracluster act are easily determined from the phase trajectories of the oxidant consumption and reaction product formation processes.

It might be expected that, upon further aggregation of Mn_2^{IV} into Mn_6^{IV} (trimerization of Mn_2^{IV}), six water molecules will be oxidized to three O_2 molecules. However, the Mn_6^{IV} clusters generate two ozone molecules rather than

three O_2 molecules. Like the Mn_2^{IV} and Mn_4^{IV} clusters, the Mn_6^{IV} cluster spends all its 12 holes in the elementary step for oxidizing six water molecules and is converted to Mn_6^{II}. At the expense of Mn^{IV} compounds, the Mn_6^{II} cluster is rapidly oxidized to Mn_6^{III}, as in the case of smaller clusters. Thus, the oxidation of water to ozone by the Mn_6^{IV} cluster is represented by the equation

$$Mn_6^{IV} + 6H_2O = Mn_6^{II} + 2O_3 + 12H^+$$

Such a reaction in manganese systems was observed for the first time by Dzhabiev *et al.*[84]

It is worth noting that the Mn_{12}^{IV} cluster also oxidizes 12 water molecules to four ozone molecules. However, the Mn_8^{IV} cluster, next to the Mn_6^{IV} cluster in size, oxidizes water to oxygen, like the Mn_4^{IV} cluster, rather than to ozone. Although the reduction of Mn_8^{IV} in the elementary intracluster act generates four O_2 molecules (as demonstrated by the phase trajectory of O_2 generation), it can be assumed that the reaction actually produces two oxozone (O_4) molecules, which are converted to four oxygen molecules in a time of the order of 10^{-12} s.[87] Such many-electron reactions have not heretofore been observed. Ozone forms in the coordination sphere of the Mn_6^{IV} and Mn_{12}^{IV} clusters, which presumably have hexagonal structures, whereas oxygen is generated by cubic clusters (Mn_4^{IV} is a cubane; Mn_8^{IV} is a dimer of cubanes; Mn_{16}^{IV} is a tetramer of cubanes; Mn_6^{IV} is a trigonal prism resembling a prismane, one of the benzene isomers; Mn_{12}^{IV} is a hexagonal prism).[84]

As noted above, in going from the smallest cluster Mn_2^{IV} to Mn_4^{IV}, the Mn^{IV} reduction and oxygen formation rate constants increase by more than an order of magnitude. It was of interest to reveal an analogous tendency for water oxidation to ozone. We have measured the reduction activation energies of the Mn_6^{IV} and Mn_{12}^{IV} clusters, which oxidize six and twelve water molecules to, respectively, two and four ozone molecules. The activation energy of the reaction for the Mn_{12}^{IV} cluster, $E_{12} = 68$ kJ mol^{-1}, turned out to be considerably lower than for the Mn_6^{IV} cluster ($E_6 = 98$ kJ mol^{-1}).[88] Thus, the manganese clusters are not only the catalysts of non-complementary chemical processes (since they make it possible to overcome the stoichiometric limitations), but also are capable of activating concerted multisubstrate reactions so that their activation energies are decreased.

Once the water oxidation to ozone has been revealed in the functional chemical model of Mn-co, we have searched for the same process in photosynthetic organisms. It has been demonstrated that water oxidation to O_3 occurs in some red (*Phyllophora nervosa*, *Polysiphonia elongata*, *Callithamnion corymbosum*)[89,90] and brown (*Cystoseira barbata*)[90] marine algae under water deficiency conditions. We explain this reaction by the fact that hexanuclear Mn-co (rather than tetranuclear) appear in dried algae, which is responsible for the capacity to oxidize three water molecules to ozone, as in the model system based on sulfuric acid manganese(IV) solutions.

Thus, the functional chemical model of Mn-co exemplifies that the polynuclearity of the metal cofactor is necessary not only for overcoming the stoichiometric limitations but also for realizing concerted multisubstrate processes, the activation energies of these processes decreasing with an increase in the number of activated substrates.

It is worth noting that the catalytic oxidation of water is of great interest to researchers, and the number of publications on the subject constantly increases. In addition, there is no shortage of reviews on different types of catalysts. For the past 30 years, the binuclear tris(bipyridyl)ruthenium catalyst (so-called blue dimer), used for elucidating the water oxidation mechanism, has been studied in detail. Recently, however, various researchers engaged in exploring ruthenium catalysts are increasingly talking about the oxidation of water by mononuclear complexes, and this is difficult to accept.

We have studied the kinetics of water oxidation by Ce^{4+} ions in the presence of the binuclear ruthenium complex $K_4[Ru_2(SO_4)_2(\mu\text{-}SO_4)_2(\mu\text{-}O)_2]\cdot 2H_2O$, an analogue of blue dimer, free of organic ligands, which deteriorate the catalyst activity and stability.[91] The results demonstrate that even binuclear complexes are not catalytically active. To exhibit activity, these complexes have to become larger up to tetranuclear or even octanuclear clusters. Even trinuclear complexes have to self-organize into large clusters in order to become catalytically active. In particular, the trinuclear complex $(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5Cl_7$ becomes an active catalyst only after its tetramer, *i.e.*, a dodecanuclear cluster, has been formed.[91–93]

Our experience shows that active catalysts are always clusters of a transition metal, be it manganese, cobalt or ruthenium. With an increase in the number of activated water molecules, the activation energy of the reaction is, as a rule, reduced. It is worth noting that the most promising new catalysts bound to polyoxometallate ligands also contain four ruthenium or cobalt atoms:[94–97] $[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$ or $[Co_4O_4(H_2O)_2.(PW_9O_{34})_2]^{10-}$. Rigid fixation of the tetranuclear ruthenium and cobalt clusters by polyoxometallate ligands accounts for the rather high stability and activity of these catalysts. Therefore, they do not assemble into large clusters, but nevertheless are capable of eight-electron oxidation of water to oxozone, like the above bi- and trinuclear ruthenium clusters, as shown by our preliminary experiments on water oxidation by cerium(IV) ions.[98] As we can see, notwithstanding the undoubted outstanding achievements in the synthesis of promising catalysts for many-electron oxidation of water, there is no single point of view on the mechanism of the processes. In this regard, there are still unsolved problems.

VII. Conclusions

Of the four key stages of natural photosynthesis, which should constitute photocatalytic converters of solar energy to the potential energy of chemical bonds, two stages can be considered completely developed. First of all, this is the photosynthetic antenna model where either several dyes are used to cover the visible range of solar radiation (as has been done in our works) or, which is even better, a specially synthesized individual photosensitizer is used that absorbs in almost the entire visible range (Grätzel and co-workers[55]). The conversion of one-electron reducing agents to hydrogen also presents no problems. As for the catalysts of many-electron water oxidation, these chemical models still have a number of unsolved issues concerning the mechanism of the process.

However, the task of creating an analogue of the crucial stage of 'artificial photosynthesis' — photoinduced charge

separation and stabilization — is almost completely unresolved. This will require more efforts to get closer to the record quantum yields demonstrated by nature. At the same time, once this problem is solved, artificial photosynthesis will immediately transform from the obvious outsider into a leader with great prospects in the utilization of solar energy.

In our opinion, for the oxidation of water by one-electron oxidants, one should select cluster catalysts that activate several water molecules at a time and generate higher molecular weight products as compared with oxygen (for example, ozone or oxozone) in their coordination sphere. Naturally, oxozone will be immediately converted to oxygen, but it will be generated in a many-electron reaction with reduced activation energy. Undoubtedly, photosynthesis should be studied comprehensively, since thanks to it we have no shortage of oxygen — the basis of all life on Earth.[99]

This review was prepared with financial support of the Division of Chemistry and Materials Science of the Russian Academy of Sciences (Programme No. 1).

References

1. N Armaroli, V Balzani *Angew. Chem., Int. Ed.* **46** 52 (2007)
2. K Zweibel, J Mason, V Fthenakis *Sci. American* **298** (1) 64 (2008)
3. V Fortov *V Mire Nauki* (1) 52 (2007)
4. N N Semenov, in *Izbrannye Trudy* (Selected Works) Vol. 4 (Moscow: Nauka, 2006) p. 231
5. Zh I Alferov *Vestn. Russ. Akad. Nauk* **79** 607 (2009) [a]
6. B N Kuzyk *Al't. Energ. Ekol.* (2) 21 (2007) [b]
7. S D Varfolomeev, I I Moiseev, B F Myasoedov *Vestn. Russ. Akad. Nauk* **79** 595 (2009) [a]
8. V M Andreev *Al't. Energ. Ekol.* (2) 93 (2007) [b]
9. V P Skulachev, V A Shuvalov *Vestn. Russ. Akad. Nauk* **76** 437 (2006) [a]
10. I I Moiseev, N A Plate, S D Varfolomeev *Vestn. Russ. Akad. Nauk* **76** 427 (2006) [a]
11. V A Pivnyuk V *Mire Nauki* (4) 88 (2008)
12. V V Eremin *Priroda* (4) 22 (2010)
13. D S Rozhdestvenskii *Izv. Akad. Nauk SSSR, Ser. Fiz.* 208 (1936)
14. A N Terenin *Izbrannye Trudy* (Selected Works) Vol. 2 (Moscow: Nauka, 19746)
15. I A Tarchevskii *Osnovy Fotosinteza* (Foundations of Photosynthesis) (Moscow: Vysshaya Shkola, 1977)
16. A E Shilov, T S Dzhabiev, in *Biokonversiya Solnechnoi Energii* (Bioconversion of Solar Energy) (Pushchino: Scientific Centre of Biological Investigations, Academy of Sciences of the USSR, 1984) p. 22
17. D O Hall *Solar Eenergy* **22** 307 (1979)
18. E Rabinowitch, Govindjee *Photosynthesis* (New York, London, Sydney, Toronto: Academic Press, 1969)
19. V A Shuvalov, A A Krasnovskii *Biofizika* **24** 544 (1981) [c]
20. A Cuni, X Lin, F Sayre, F Rappaport, J Lavergne *Phys. Chem. Chem. Phys.* **6** 4825 (2004)
21. P Joliot, B Kok, in *Bioenergetics of Photosynthesis* (Ed. Govindjee) (New York: Academic Press, 1975) p. 387
22. S V Khangulov, M G Goldfeld, L A Blyumenfeld *Dokl. Akad. Nauk SSSR* **218** 726 (1974) [d]
23. A A Krasnovskii, G P Brin *Dokl. Akad. Nauk SSSR* **147** 656 (1962) [d]
24. A A Krasnovskii, G P Brin *Dokl. Akad. Nauk SSSR* **168** 1100 (1966) [d]
25. A A Krasnovskii, G P Brin, in *Molekulyarnaya Fotonika* (Molecular Photonics) (Ed. A A Krasnovskii) (Leningrad: Nauka, 1970) p. 161
26. G V Fomin, G P Brin, M V Genkin, A A Krasnovskii, L A Blyumenfeld *Dokl. Akad. Nauk SSSR* **212** 424 (1973) [d]
27. G A Korsunovskii, in *Elementarnye Fotoprotsessy v Molekulakh* (Elementary Photoprocesses in Molecules) (Ed. B S Neporent) (Moscow, Leningrad: Nauka, 1966) p. 139
28. A A Krasnovskii *Vestn. Akad. Nauk SSSR* 83 (1979) [a]
29. P M Kruglyakov, Yu G Rovin *Fizikokhimiya Chernykh Uglevodorodnykh Plenok* (Physical Chemistry of Black Hydrocarbon Films) (Moscow: Nauka, 1978)
30. J H Fendler *Membrane Mimetic Chemistry* (New York: Wiley, 1982)
31. S D Varfolomeev *Konversiya Energii Biokataliticheskimi Sistemami* (Conversion of Energy by Biocatalytic Systems) (Moscow: Moscow State University, 1981)
32. E N Kondrat'eva, I N Gogotov *Molekulyarnyi Vodorod v Metabolizme Mikroorganizmov* (Molecular Hydrogen in Metabolism of Microorganisms) (Moscow: Nauka, 1981)
33. J W Newton *Science* **191** 559 (1976)
34. J R Benemann, J A Berenson, N O Kaplan, M D Kamen *Proc. Natl. Acad. Sci. USA* **70** 2317 (1973)
35. P Candau, C Manzano, M Losada *Nature (London)* **262** 715 (1976)
36. J R Bolton *J. Solid State Chem.* **22** 3 (1977)
37. K I Zamaraev, V N Parmon *Russ. Chem. Rev.* **49** 695 (1980) [*Usp. Khim.* **49** 1457 (1980)]
38. V I Laptev *Dokl. Akad. Nauk* **430** 780 (2010) [e]
39. T S Dzhabiev, V A Nadtochenko, I V Rubtsov, V A Smirnov *Dokl. Akad. Nauk SSSR* **294** 1401 (1987) [d]
40. M V Volkenshtein *Biofizika* (Biophysics) (St Petersburg: Lan', 2008)
41. T A Moore, A L Moore, D Gust *Philos. Trans. R. Soc. London, Ser. B* **357** 1481 (2002)
42. Y Kobuke *Eur. J. Inorg. Chem.* 2333 (2006)
43. R F Kelley, M J Tauber, M R Wasielewski *J. Am. Chem. Soc.* **128** 4779 (2006)
44. E G Andrizhiyevskaya, D Frolov, R van Grondelle, J P Dekker *Phys. Chem. Chem. Phys.* **6** 4810 (2004)
45. C-Y Chen, J-G Chen, S-J Wu, J-Y Li, C-G Wu, K-C Ho *Angew. Chem., Int. Ed.* **47** 7342 (2008)
46. W M Campbell, K W Jolley, P Wagner, K Wagner, P J Walsh, K C Gordon, L Schmidt-Mende, M K Nazeeruddin, Q Wang, M Grätzel, D L Officer *J. Phys. Chem. C* **111** 11760 (2007)
47. H Choi, C Baik, S O Kang, J Ko, M-S Kang, M K Nazeeruddin, M Grätzel *Angew. Chem., Int. Ed.* **47** 327 (2008)
48. A Staniszewski, W B Heuer, G J Meyer *Inorg. Chem.* **47** 7062 (2008)
49. F Gao, Y Wang, D Shi, J Zhang, M Wang, X Jing, R Humphry-Baker, P Wang, S M Zakeeruddin, M Grätzel *J. Am. Chem. Soc.* **130** 10720 (2008)
50. H Choi, S Kim, S O Kang, J Ko, M-S Kang, J N Clifford, A Fornelli, E Palomares, M K Nazeeruddin, M Grätzel *Angew. Chem., Int. Ed.* **47** 8259 (2008)
51. C Lee, J-H Yum, H Choi, S O Kang, J Ko, R Humphry-Baker, M Grätzel, M K Nazeeruddin *Inorg. Chem.* **47** 2267 (2008)
52. D Kuang, S Uchida, R Humphry-Baker, S M Zakeeruddin, M Grätzel *Angew. Chem., Int. Ed.* **47** 1923 (2008)
53. W H Howie, F Claeyssens, H Miura, L M Peter *J. Am. Chem. Soc.* **130** 1367 (2008)
54. D Gust, T A Moore, A L Moore *Acc. Chem. Res.* **42** 1890 (2009)
55. T Bessho, S M Zakeeruddin, C-Y Yeh, E W-G Diau, M Grätzel *Angew. Chem., Int. Ed.* **49** 6646 (2010)
56. *Oksredmetriya* (Oxredmetry) (Ed. B P Nikol'skii, V V Pal'chevskii) (Leningrad: Khimiya, 1975)

57. A L Rotinyan, K I Tikhonov, I A Shoshina *Teoreticheskaya Elektrokhimiya* (Theoretical Electrochemistry) (Moscow: Mir, 1981)
58. B A Kiselev, V B Evstigneev, I G Tsygankova *Dokl. Akad. Nauk SSSR* **230** 726 (1976) [d]
59. M Yokoyama, S Shimokihara, A Matsubara, H Mikawa *Polym. J.* **14** 77 (1982)
60. T S Dzhabiev *Dokl. Akad. Nauk SSSR* **257** 1169 (1981) [d]
61. H T Witt *Biochim. Biophys. Acta* **505** 355 (1979)
62. Yu Ya Gurevich, Yu V Pleskov, in *Elektrokhimiya (Itogi Nauki i Tekhniki)* [Electrochemistry (Advanced in Science and Engineering)] (Moscow: Izd. VINITI, 1982) Vol. 18, p. 3
63. V Ya Shafirovich, Doctoral Thesis in Chemical Sciences, Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, 1987)
64. J Wiberg, L Guo, K Pettersson, D Nisson, T Ljungdahl, J Mårtensson, B Albinsson *J. Am. Chem. Soc.* **129** 155 (2007)
65. R Carmieli, Q Mi, A B Ricks, E M Giacobbe, S M Mickley, M R Wasielewski *J. Am. Chem. Soc.* **131** 8372 (2009)
66. J R Benemann *J. Appl. Phycol.* **12** 291 (2000)
67. A A Krasnovskii, V V Nikandrov, G P Brin, I N Gogotov, V P Oshchepkov *Dokl. Akad. Nauk SSSR* **225** 711 (1975) [d]
68. P H Homann *Photosynth. Res.* **76** 93 (2003)
69. A Melis *Planta* **226** 1075 (2007)
70. G-P Sheng, H-Q Yu, C-M Wang *Appl. Microbiol. Cell Physiol.* **73** 204 (2006)
71. L Zhang, A Melis *Philos. Trans. R. Soc. London, Ser. B* **357** 1499 (2002)
72. J H Jo, D S Lee, J M Park *Biotechnol. Prog.* **22** 431 (2006)
73. H Ozawa, M Haga, K Sakai *J. Am. Chem. Soc.* **128** 4926 (2006)
74. E D Cline, S E Adamson, S Bernhard *Inorg. Chem.* **47** 10378 (2008)
75. B Probst, C Kolano, P Hamm, R Alberto *Inorg. Chem.* **48** 1836 (2009)
76. A Fihri, V Artero, M Razavet, C Baffert, W Leibl, M Fontecave *Angew. Chem., Int. Ed.* **47** 564 (2008)
77. K Watanabe, S Takizawa, S Murata *Chem. Lett.* **40** 345 (2011)
78. A L Stroyuk, A E Raevskaya, A V Korzhak, I E Kotenko, E M Glebov, V F Plyusnin, S Ya Kuchmii *Teor. Eksp. Khim.* **45** 8 (2009) [f]
79. J Yano, V K Yachandra *Inorg. Chem.* **47** 1711 (2008)
80. F Liu, J J Concepcion, J W Jurss, T Cardolaccia, J L Templeton, T J Meyer *Inorg. Chem.* **47** 1727 (2008)
81. J P McEvoy, G W Brudvig *Chem. Rev.* **106** 4455 (2006)
82. R Eisenberg, H B Gray *Inorg. Chem.* **47** 1697 (2008)
83. T S Dzhabiev, V Y Shafirovich, A E Shilov *React. Kinet. Catal. Lett.* **4** 11 (1976)
84. T S Dzhabiev *Kinet. Katal.* **51** 816 (2010) [g]
85. D A Frank-Kamenetskii *Diffuziya i Teploperedacha v Khimicheskoi Kinetike* (Diffusion and Heat Transfer in Chemical Kinetics) (Moscow: Nauka, 1967)
86. L S Pontryagin *Obyknovennye Differentsial'nye Uravneniya* (Ordinary Differential Equations) (Moscow: Nauka, 1970)
87. N P Lipikhin *Russ. Chem. Rev.* **44** 637 (1975) [*Usp. Khim.* **44** 1366 (1975)]
88. T S Dzhabiev, G A Kurkina *Al't. Energ. Ekol.* (6) 94 (2007) [b]
89. T S Dzhabiev, D N Moiseev, A E Shilov *Dokl. Akad. Nauk* **402** 555 (2005) [d]
90. G A Kurkina, Candidate Thesis in Chemical Sciences, Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, 2008
91. M L Temnova, Z M Dzhabieva, in *Uspekhi Khimicheskoi Fiziki (Sb. Tez. Dokl. na Vseros. Molodezhnoi Konferentsii)* [Progress in Chemical Physics (Abstracts of Reports on All-Russian Youth Conference), Chernogolovka, 2011] p. 106
92. Z M Dzhabieva, A A Skladanyuk, T S Dzhabiev, in *XVIII Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii (Tez. Dokl.)* [The XVIIIth Mendeleev Congress on General and Applied Chemistry (Abstracts of Reports)] Moscow, 2007] Vol. 3, p. 336
93. M L Temnova, Z M Dzhabieva, in *Uspekhi Sinteza i Kompleksoobrazovaniya (Tez. Dokl. Vseros. Nauchnoi Konferentsii s Mezhdunarodnym Uchastiem, Posvyashchennoi Mezhdunarodnomu Godu Khimii)* [Progress in Synthesis and Complex Formation (Abstracts of Reports of All-Russian Scientific Conference with International Participation Devoted to International Year of Chemistry), Moscow, 2011] p. 336
94. Y V Geletii, Z Huang, Y Hou, D G Musaev, T Lian, C L Hill *J. Am. Chem. Soc.* **131** 7522 (2009)
95. Z Huang, Z Luo, Y V Geletii, J W Vickers, Q Yin, D Wu, Y Hou, Y Ding, J Song, D G Musaev, C L Hill, T Lian *J. Am. Chem. Soc.* **133** 2068 (2011)
96. G Süss-Fink *Angew. Chem., Int. Ed.* **47** 5888 (2008)
97. C Besson, Z Huang, Y V Geletii, S Lense, K I Hardcastle, D G Musaev, T Lian, A Proust, C L Hill *Chem. Commun.* **46** 2784 (2010)
98. N Yu Shmatko, Z M Dzhabieva, in *Uspekhi Khimicheskoi Fiziki (Sb. Tez. Dokl. na Vseros. Molodezhnoi Konferentsii)* [Progress in Chemical Physics (Abstracts of Reports on All-Russian Youth Conference), Chernogolovka, 2011] p. 109
99. D G Zamolodchikov *Vestn. Russ. Akad. Nauk* **76** 209 (2006) [a]

[a] — *Herald Russ. Acad. Sci. (Engl. Transl.)*
[b] — *Int. Sci. J. Altern. Energ. Ecol. (Engl. Transl.)*
[c] — *Biophysics (Engl. Transl.)*
[d] — *Dokl. Biochem. Biophys. (Engl. Transl.)*
[e] — *Dokl. Phys. (Engl. Transl.)*
[f] — *Theor. Exp. Chem. (Engl. Transl.)*
[g] — *Kinet. Catal. (Engl. Transl.)*