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Molecular Photocatalytic Systems for Solar Energy Conversion: Catalysts for the Evolution of Hydrogen and Oxygen from Water †

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This review is devoted to recent advances in the development and study of homogeneous and heterogeneous catalysts for the reduction of water to molecular hydrogen and its oxidation to molecular oxygen. The production of micro-heterogeneous systems for photocatalytic charge separation is also discussed. 114 references.

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I. INTRODUCTION

Mankind's total annual energy consumption now stands at the enormous value of ~10^{17} kcal, and is still rising rapidly, doubling every 15–20 years[1–3]. However, our reserves of mineral fuels which provide the main input to the energy balance (~80% of the primary energy resources, including ~60% of petroleum and gas) are strictly limited: the total energy equivalent of the explored reserves of these fuels is estimated to be[3–5] 10^{19}–10^{20} kcal. Thus the search for alternative sources of energy is a very important problem.

It is thought that for the immediate future the energy requirements of the world community will be satisfied by an increase in the mining and conversion of coal (including its conversion into artificial liquid fuel), and in the use of nuclear sources of electrical energy and heat. The raw materials required by these two branches of energetics are assured for at least one century. In both cases the level of scientific and technological development already reached is high enough to make early practical exploitation a real possibility. However, we should not forget that a substantial increase in the use of coal and of nuclear fuel will present a number of as yet unsolved problems arising from possibly detrimental effects on the environment. For example, the combustion and treatment of coal will require the development of cheap purification plant to prevent the accumulation of sulphur oxides, carcinogens, and other harmful substances in the atmosphere. There is even a danger that at the expected rate of increase of energy

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consumption the anthropogenic heat evolution from the use of fossil and nuclear fuels may reach several per cent of the total heat balance of the Earth by the middle of the next century, with unpredictable effects on the Earth's climate[6]. Equally unpredictable are the consequences of enriching the atmosphere in carbon dioxide (unavoidably produced by the combustion of organic substances).

For the more distance future we must look to two sources of energy available almost without limit: thermo-nuclear energy and solar energy[1]. Neither of these sources can yet be widely exploited because the level of scientific and technological development is inadequate at present in both cases. However, there is every reason to expect very rapid progress. Basic research on a controlled thermo-nuclear reaction is in progress. Although this reaction has not yet been realised experimentally, the potential advantages of thermo-nuclear synthesis as a source of energy have been widely discussed for many years. On the other hand the possibilities offered by solar energy are less clearly characterised, though it is known that the energy content of the Sun's rays which reach the Earth is far in excess of even the highest estimates of mankind's increasing requirements[1-3,7,8]. The only problem is to learn how to use this energy effectively.

There can be no doubt that in the near future the traditional sources of energy will continue to play a major role in the overall energy balance of mankind. Nevertheless, even the International Energy Conference (an organisation traditionally opposed to the use of solar energy) admits the possibility of a significant increase in the direct exploitation of solar energy: in particular, it is expected that by the year 2020 up to 10–15% of the world's energy requirements will be provided by solar energy converters[2].

One of the most promising methods of utilising solar energy is its direct conversion into chemical fuel energy[1,9-11]. Storing the Sun's energy in the form of chemical fuels would overcome the most serious obstacle to the widespread use of solar energy (its dependence on seasonal, meteorological, and other natural conditions) as well as making the energy available in a more concentrated and generally usable form (a high-level chemical energy source).

In principle any chemical process in which free energy is accumulated can be used for the conversion of solar energy. The most attractive, at present, are the reactions which produce high-energy fuels (hydrogen, hydrocarbons, alcohols and carbohydrates, hydrazine, ammonia, etc.) from water and atmospheric gases, which offer a readily available and almost inexhaustible raw material (see, for example, the recent reviews in Refs.12 and 13). The advantages of these reactions include the high energy content of the resulting fuel (the combustible–oxidiser (oxygen) pair of chemical substances), and also the possibility in principle of achieving a relatively high efficiency (up to ~30%) in the conversion of solar energy[14-16]. We should stress that the production of all these fuels takes place *in vivo* in plants and micro-organisms (either by photosynthesis, followed by fermentation of the products to hydrogen, methane, alcohols, etc., or by atmospheric nitrogen fixation).

However, these reactions do not proceed spontaneously in sunlight outside the living organism. They require the development of *photocatalytic* systems, consisting of *photocatalysts* (for the photochemical step) and *ordinary catalysts* (for the subsequent dark reaction steps giving the energy-rich chemical substances).

Photocatalysts are substances which can induce (by the absorption of light quanta) chemical reactions between the components of a reaction by undergoing repeated chemical interactions to form an intermediate and regenerating themselves after each interaction. (The term "photocatalyst" is often replaced, in published papers, by the term "photosensitiser", on the assumption that the two are synonymous. It would be more correct to reserve the term "photosensitiser" for substances which induce reactions by energy transfer to the reactants rather than by forming chemical intermediates with them.)

The most interesting of the fuel-producing processes listed above is the production of hydrogen by the decomposition of water. Hydrogen is one of the preferred (and ecologically clean) chemical fuels for energy production in the future. It is also a valuable raw material for the chemical industry, used in large quantities for the catalytic reduction of carbon dioxide and molecular nitrogen to give all the fuels listed above. Lastly, existing information on the chemical reaction mechanisms suggests that the photocatalytic decomposition of water should be the most easily realisable of all the reactions for storing solar energy as fuels.

Some definite advances in the development of photocatalytic systems for the decomposition of water into hydrogen and oxygen have already been reported. The systems can arbitrarily be classified into two groups: semiconductor systems and molecular systems.

Semiconductor systems rely on massive or on finely divided semiconductors as photocatalysts (mainly oxides, phosphides, arsenides and chalcogenides of the transition metals). By using these substances solar energy has been converted into chemical fuel energy with reasonable efficiencies (up to 1–2%) (see the pioneering paper by Fujishima and Honda[17], and also the most recent reviews[18-21] and their references). The efficiency of semiconductor photocatalytic systems for the decomposition of water will probably be further increased by research now in progess. A detailed analysis of the present situation in the field of semiconductor photocatalysis will be found in the same reviews[18-21].

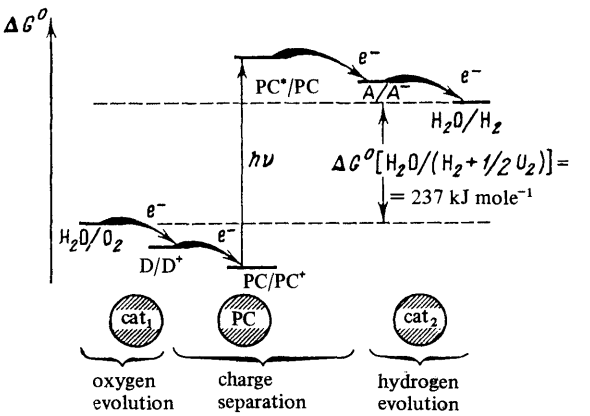


Figure 1. Energy diagram for the decomposition of water in a molecular photo-catalytic system; ΔG° is the change in free energy for the process, the curved arrows show the electron transfer paths.

Molecular photocatalytic systems attempt to reproduce (or model) the natural photosynthesis schemes. Work on these systems began later than on the semiconductor systems,

and has not yet produced really significant advances. However, since we know that the efficiency of the conversion of solar energy by the molecular systems used in natural photosynthesis is quite high (up to 6–10% for the relatively complex reaction between CO_2 and H_2O [22,23]) there is every reason to expect the early development of efficient artifical converters for the much simpler water decomposition reaction.

Recent progress in the development of molecular photocatalytic systems for the decomposition of water have been discussed in a number of reviews[21,24–29], including one by the present writers[12]. Among the papers published since our review[12] the most noteworthy are Refs.30 and 31 (see also Refs.21 and 25), which claim the development of the first artificial molecular system capable of yielding the full cycle of decomposition of water into hydrogen and oxygen under the influence of visible light (albeit with a modest efficiency).

The water decomposition schemes most often considered include three steps (see Fig.1): charge separation, i.e. the production (under the influence of light and in the presence of the photocatalyst PC) of relatively strong chemical oxidisers (D^+) and reducers (A^-)

$$D + A \xrightarrow[PC]{h\nu} D^+ + A^- \qquad (1)$$

followed by catalytic processes for the evolution from water of oxygen by the oxidisers D^+

$$4D^+ + 2H_2O \xrightarrow{cat_1} 4D + 4H^+ + O_2\uparrow \qquad (2)$$

and of hydrogen by the reducers A^-

$$2A^- + 2H^+ \xrightarrow{cat_2} 2A + H_2\uparrow . \qquad (3)$$

Light is not needed for the last two steps. The overall process is described by the equation

$$2H_2O \xrightarrow[cat_1,\ cat_2]{h\nu,\ PC,\ D,\ A} 2H_2 + O_2 .$$

Thus efficient catalysts of three types must be developed in order to realise the decomposition of water into hydrogen and oxygen by sunlight in the presence of a molecular photocatalytic system: catalysts for charge separation in visible light, catalysts for oyxgen evolution from water by one-electron oxidisers, and catalysts for hydrogen evolution from water by one-electron reducers. For example, in the proposed[30,31] molecular photocatalytic system the compounds PC, A, cat_1, and cat_2 are, respectively, the *tris*-bipyridyl complex of ruthenium(II) [$Ru(bipy)_3^{2+}$], the organic bication *N,N'*-dimethyl-4,4'-dipyridine ("methylviologen", MV^{2+}), colloidal ruthenium dioxide, and colloidal platinum. The photocatalyst PC also acts as the intermediate donor D.

In this review we shall discuss the main results of recent work carried out in our laboratory since the publication of our last review[12] on the development and characterisation of catalysts for all three steps in the decomposition of water by molecular photocatalytic systems: we shall begin with the hydrogen evolution step, which is the most developed at present.

II. EVOLUTION OF HYDROGEN FROM WATER

The one-electron reducers A^- formed in the charge separation step [reaction (1)] can evolve hydrogen from water by reaction (3) only in the presence of special catalysts. Even the earliest workers[32–38] had suggested several possible catalysts for this process: supported[39–41] or colloidal precious metals (references given below), and biological enzymes (hydrogenase and nitrogenase[28,34,39,42–48]). To compare the relative merits of these catalysts in practical photocatalytic systems we need detailed quantitative information on their catalytic activity and stability, and also on the dependence of these properties on the formation conditions of the catalyst. Studies of this type are now being made in a number of laboratories on colloidal metal catalysts (see, for example, Refs.21 and 41–56, and their lists of references).

In the following sections we shall discuss two types of catalyst for the evolution of hydrogen from water: 1) highly dispersed precious metals, stabilised in polymer globules and grandules which are permeable to the reducing agent and to water molecules, and 2) heteropolyanions (compounds containing several transition metal ions which can be fully and reversibly reduced by accepting two or more electrons). Thus the heteropolyanions can be treated as structural and functional models of the hydrogenase and nitrogenase enzymes, whose active centres also contain several transition metal ions and are reduced reversibly by several electrons.

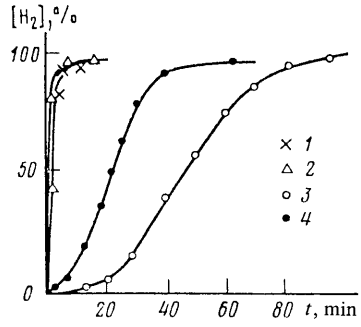


Figure 2. Kinetics of hydrogen evolution (in per cent of the stoichiometric yield) from a 1.5×10^{-2} M solution of VSO_4 in water in the presence of various catalysts: *1*) [Rh·en]Cl_3, *2*) and *3*) Rh–PEI of composition Rh : N ≅ 1 : 2 and 1 : 4 respectively, *4*) [$Rh(en)_2Cl_2$](ClO_4). Volume of solutions 20 cm^3, amount of rhodium in solution ~10^{-5} g-atom, pH of solutions adjusted to pH : 0 by H_2SO_4, temperature 298 K.[57]

1. The Rhodium–Ethylenediamine and Rhodium–Polyethyleneimine Systems

We have shown[57] that the coordinationally unsaturated complexes of rhodium(III) with ethylenediamine (en) and with its polymeric analogues (polyethyleneimines) are active catalysts for the evoluation of hydrogen from water by one-electron reducers such as V^{2+}(aq), Cr^{2+}(aq), and the cation radical methylviologen (MV^{+}), by the reaction

$$2A^- + 2H^+ \xrightarrow{cat_2} 2A + H_2\uparrow$$

or

$$2A^- + 2H_2O \xrightarrow{cat_2} 2A + H_2\uparrow + 2OH^- \qquad (3a)$$

The most interesting in practice are the heterogeneous catalysts based on polymers: branching polyethyleneimine (PEI) of molecular weight ~20 000 and the commercial ion exchanger AN-221 (granulated, partially cross-linked polyethyleneimine).

Studies by ESR, X-ray photo-electron spectroscopy (XPS), and optical spectroscopy in the visible and u.v. regions have shown[58] that in the initial forms of the catalyst based on monomeric ethylenediamine almost the whole of the rhodium is present as the rhodium(III) complex, whereas in catalysts based on polyethyleneimine up to 5% of the rhodium (depending on the preparative conditions) can be present as a rhodium(II) compound, the remainder being in the form of a rhodium(III) compound. It was shown that whereas with monomeric ligands the initial complexes can have the composition Rh : N = 1 : 6, 1 : 4, and 1 : 2 (the latter complexes being obtained only in mixtures with Rh : N = 1 : 4 complexes), in the case of polymeric deprotonated ligands initial complexes of composition Rh : N = 1 : 4 and 1 : 2 are formed. By varying the metal–ligand ratio in the synthesis we can obtain heterogenised metal–polymer complexes predominantly of the Rh : N = 1 : 2 or 1 : 4 composition.

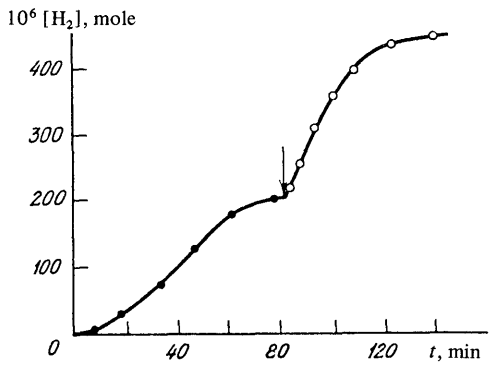


Figure 3. Kinetics of the evolution of hydrogen from a 1.5×10^{-2} M solution of VSO_4 in water in the presence of the polymer catalyst Rh–PEI of composition Rh : N ≅ 1 : 4; other conditions as in Fig. 2, the arrow denotes the addition of the second portion of VSO_4.

The addition of complexes of rhodium with ethylenediamine or polyethyleneimine to solutions of reducing agents such as V^{2+}(aq) (redox potential $E_0 = -0.25$ V relative to the NHE) and Cr^{2+}(aq) ($E_0 = -0.4$ V) causes evolution of molecular hydrogen. Typical H_2 evolution kinetic curves are shown in Fig. 2. They are S-shaped, with an initial induction period during which the reaction gradually accelerates. The induction period probably corresponds to the formation of the active forms of the catalyst (possibly highly dispersed particles of metallic rhodium, see below). The slowing down of the reaction at long times indicates depletion of the reducing agent. Thus, at the plateau of Fig. 2 the amount of hydrogen evolved is almost exactly 100% of stoichiometric for reaction (3) or (3a). At the same time by adding reducing agent at its original concentration when the reaction has come to an end we can produce a renewed evolution of hydrogen in which the slope of the kinetic curve is either the same as that of the initial curve or greater (see Fig. 3). As Fig. 2 shows, both with the monomeric and with the polymeric ligand the activated catalysts prepared from complexes of composition Rh : N = 1 : 2 have a much higher activity than those prepared from complexes of composition Rh : N = 1 : 4. In the presence of monomeric coordinationally unsaturated complexes of composition Rh : N = 1 : 6 no hydrogen is evolved by the reaction with V^{2+}(aq) or Cr^{2+}(aq).

According to X-ray structural analysis and XPS results[58] the activation of the monomer complexes of composition Rh : N = 1 : 2 causes complete reduction to finely divided metallic rhodium. The formation of a phase of metallic rhodium of very small particle size was observed also in all the activated polymer catalysts. Electron microscopic studies of the particles of metallic rhodium in polymer catalysts revealed a complex size distribution, depending on the catalyst preparation conditions. However, in every case we can detect a large number of small (10–30 Å) particles partially coalescing into larger and irregular formations. Evidently, the metallic rhodium is responsible for the catalytic activity of all the catalysts based on ethylenediamine and polyethyleneimine.

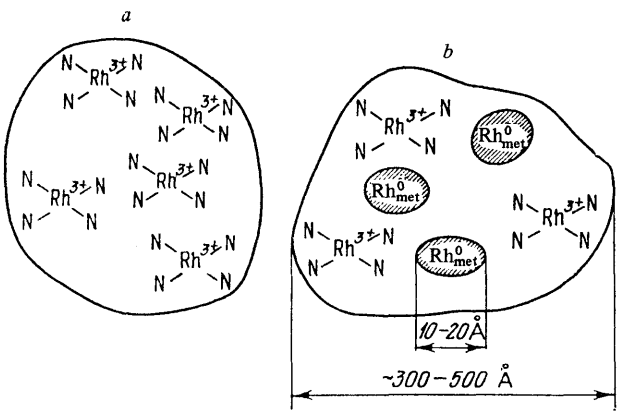


Figure 4. Structure of the Rh–PEI catalyst of composition Rh : N ≅ 1 : 4 (*a*) before and (*b*) after activation.

However, in the activated polyethyleneimine catalysts of composition Rh : N = 1 : 4 not all the rhodium ions are reduced to the metal. The reflection spectra of these catalysts in the u.v. and visible regions indicate the presence of large amounts of unchanged initial complexes of composition Rh : N = 1 : 4.[58] The XPS spectra also suggest that most of the rhodium on the sample surface is in the form of Rh^{3+} ions rather than of metal. A schematic model of the activated catalysts consistent with the results of various physicochemical methods of analysis is shown in Fig. 4. We note that the size of the finely divided metal particles in the polymer globule is strongly dependent on the catalyst activation conditions. Thus, an increase in the pH of the solution in which activation takes place causes a marked decrease in particle size.

The maximum rate (α) of hydrogen evolution (i.e. the rate in the region of maximum slope of the S-shaped kinetic curves) referred to 1 g-atom of added rhodium[59] was taken as the quantitative characteristic of the catalytic activity. Values of α for catalysts prepared by different methods are compared in Table 1. In the case of the most active catalysts

(Nos.7, 8, 11, 12) the tabulated value is not the parameter α but its lower limit. This is because reaction (3) had almost gone to completion when the first gas sample was taken for chromatographic analysis, and its rate could not be measured to better than a lower estimate.

Table 1. Catalytic activity (α, mole H_2 mole^{-1} Rh h^{-1}) of complexes of rhodium with polyamines towards the evolution of hydrogen from 1.5×10^{-2} M solutions of VSO_4 in water at 298 K (pH adjusted with H_2SO_4). [59]

No.	Initial form of catalyst	pH	$[V^{2+}]/[Rh^{3+}]$	α
1	$[Rh(en)_3](ClO_4)_3$ (Rh : N = 1 : 6)	0	30	<0.01
2	$[Rh(en)_2Cl_2](ClO_4)$ (Rh : N = 1 : 4)	0	6	5.0
3	ditto	1	6	2.9
4	»	2	6	1.6
5	»	3	6	0.75
6	»	4	6	0.15
7	$[Rh\cdot en]Cl_3$ (Rh:N≈1:2)	0—2	30	>300
8	ditto	2	240	>1700
9	Rh — PEI (Rh : N ≈ 1 : 4)	0	30	16
10	ditto	2	30	0.82
11	Rh — PEI (Rh : N ≈ 1 : 2)	0	30	>400
12	ditto	2	30	>300
13	Rh — AN-221 (~7%Rh, Rh : N ~ 1:3,4)	2	120	8.7
14	ditto	2	120	640*

*Catalytic granules ground to a powder of particle size less than 0.1 mm; initial size of the granules 2 mm.

It is clear from Table 1 that the catalysts prepared from complexes (with monomeric ligands) of composition Rh : N = 1 : 2 have an activity several orders higher than the complexes of composition Rh : N = 1 : 4 with the same ligands. The lower activity of the catalysts prepared from the latter complexes can be ascribed to the less complete conversion of the ionic forms of rhodium into highly dispersed metal particles. Thus the activation of the monomer complex of composition Rh : N = 1 : 2 is accompanied by a visible precipitation of metallic rhodium in the solution, whereas during the activation of the complexes of composition Rh : N = 1 : 4 the precipitation of metallic rhodium is undetectable.

The dependence of the catalytic activity α on the concentration of H^+ ions was studied[59] for monomer complexes of composition Rh : N = 1 : 4. We see from Table 2 that the parameter α for these catalysts increases monotonically with the concentration of H^+ in the solution where reaction (3) is taking place after activation of the catalyst. However, this increase in α is much slower than expected from the law of mass action for a reaction in which the H^+ ion appears in the rate-limiting step. Further work is needed to explain the observed dependence of α on $[H^+]$.

As in the case of the monomer complex, changing from a polymer complex with a ratio Rh : N = 1 : 4 to a polymer with Rh : N = 1 : 2 causes a large increase in catalytic activity. Again, as in the case of the monomer catalyst of composition Rh : N = 1 : 2, and for the same reason, we could only obtain a lower estimate of α for the polymers with Rh : N ≅ 1 : 2.

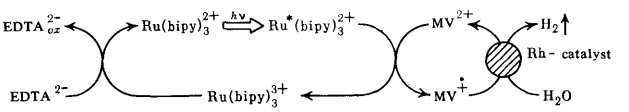
In the catalyst Rh—AN-221, consisting of granules of the AN-221 anion exchanger containing ~7% of rhodium (Rh : N = 1 : 3.4), we studied[59] the dependence of the rate of hydrogen evolution on the size of the granules and on the concentration of the catalyst and of the two reactants (H^+ and V^{2+}(aq) ions). At high enough rates of stirring of the solution, the rate of evolution of hydrogen was found to increase in proportion to the amount of catalyst (i.e. α was independent of the amount of catalyst). Thus the rate of hydrogen evolution is limited under these conditions by processes involving the catalyst, and not by mass transfer in solution or at the interface between the solution and the gas phase. However, we found a substantial increase in rate for a decrease in the particle size of the catalyst (for example, α = 8.7 for granules 2 mm in diameter and α = 640 for the same catalyst ground to a granule size of less than 0.1 mm, see Nos.13 and 14 in Table 1). This suggests rate limitation by mass transfer processes within the polymer granule rather than by the catalytic reaction.

A study[59] of the dependence of α on the concentration of V^{2+}(aq) showed an increase of α with $[V^{2+}(aq)]$ at low concentrations of V^{2+}(aq) (<5×10^{-3} M), but at higher concentrations (5×10^{-3}–2×10^{-2} M) α was independent of $[V^{2+}(aq)]$. It follows that at low concentrations of V^{2+}(aq) the process is limited by reactions involving these ions. On the other hand at high concentrations of V^{2+}(aq) the rate of this step is so high that the reaction is no longer rate-limiting. Thus the diffusion within the polymer particle of some other participant in the reaction (reactant, or product) becomes rate-limiting at these concentrations.

The dependence of α on the concentration of H^+ ions was studied only at low concentrations of V^{2+}(aq) in solutions of constant ionic strength (μ = 2 M) generated by additions of sodium sulphate: in this case the changes in α are described by the equation $\alpha \propto [H^+]^{0.2}$. The data were obtained by measuring α at different pH values for the same sample of catalyst previously activated at pH 2 and 298 K in a solution containing 10^{-2} M VSO_4 and a ratio of $[V^{2+}(aq)]/[Rh^{3+}] = 20$. Thus in this case the dependence of α on $[H^+]$ is weaker than expected from the law of mass action if the rate-limiting step involves H^+. As in the case of the monomer catalyst, further work is needed to explain the observed dependence of α on $[H^+]$ for this catalyst. However, we note that in this case the dependence could reflect the influence of H^+ ions on the structure of the polymer granule, which contains easily protonised nitrogen atoms.

It follows that at high concentrations of V^{2+}(aq) the rate of the catalytic process with rhodium catalysts in anion exchange resins is determined (most probably) by diffusion of the products of reaction (3) within the polymer granules, i.e. by the diffusion of V^{3+} cations up or of hydrogen molecules.

As expected, all these rhodium catalysts remain active when used in the classical photocatalytic system for hydrogen evolution from water with the *tris*-bipyridyl complex of ruthenium(II) (photocatalyst), methylviologen MV^{2+} (intermediate electron-transfer acceptor), and anions of ethylenediaminetetra-acetic acid $EDTA^{2-}$ (irreversibly consumed electron donor):



Throughout this review we shall use the symbol $EDTA_{ox}^{2-}$ to denote the products of irreversible oxidation of $EDTA^{2-}$.

Polymer rhodium catalysts (like other catalysts containing finely divided metals when activated) cause fairly rapid deactivation of this photocatalytic system, probably by hydrogenating the charge transfer agent MV^{2+}.

It is interesting to compare the activity of these catalysts in the evolution of hydrogen from aqueous solutions with the activity of the hydrogenase enzymes in the same reaction.

Published values of α for hydrogenase lie between 10^4 and 10^7 mole H_2 mole^{-1} of enzyme h^{-1},[48] i.e. they are much greater than the α values for catalysts based on rhodium polymer complexes. The difference becomes much smaller if we compare the α′ activities, i.e. the activities referred to unit mass of rhodium and of the enzyme (rather than to 1 mole of rhodium and of the enzyme). Thus for the more active catalysts based on an anion exchanger α′ can be as high as ~0.5 mole H_2 g^{-1} of catalyst h^{-1}, as compared with 0.2–200 mole H_2 g^{-1} of enzyme h^{-1} for hydrogenase[48].

While inferior to the best hydrogenases in catalytic activity per unit weight, the catalysts based on rhodium polymer complexes are superior in stability, especially in acid media (where hydrogenases are deactivated almost instantaneously). Furthermore, unlike hydrogenase, the activated catalysts based on anion exchangers and on PEI can be stored in air for long periods without significant loss of activity. We also note that the activity of rhodium polymer catalysts can be improved by eliminating (or decreasing) the diffusional limitations of the reaction.

Catalytic activity towards the evolution of hydrogen from water under the influence of one-electron reducing agents was observed also for the complexes of PEI with ruthenium[57], palladium, and platinum[60]. Thus catalysts for the evolution of hydrogen from water can be obtained by immobilising ions of other metals (not only rhodium) on PEI and reducing them to the metal. An important practical advantage of this type of catalyst for the future is their stability in aqueous solutions over a very wide range of pH, and their availability in the form of granules or films with controlled geometric characteristics.

2. Systems with Heteropoly Compounds

The heteropoly compounds have been identified as a potentially useful class for use in systems for evolution of hydrogen from water: as was pointed out above, they can be treated as models of the active centres in hydrogenases and nitrogenase. We know, for example, that highly reduced forms of heteropolyacids (HPA) of the 12-series have negative (or near-zero) electrochemical reduction potentials relative to the NHE, i.e. they satisfy the thermodynamic requirements for hydrogen evolution from acidic aqueous solutions. Thus the reduction potential E_0 for the acid $H_3[PMo_{12}O_{40}]$ (HPA-I) reduced by six electrons and for the acid $H_4[SiMo_{12}O_{40}]$ (HPA-II) reduced by four electrons is close to +0.1 V, whereas for the heteropolyacids reduced by two electrons $H_3[PW_{12}O_{40}]$ (HPA-III) and $H_4[SiW_{12}O_{40}]$ (HPA-IV) the E_0 values are close to 0 and −0.2 V respectively[61–63]. We have observed[64,65] spontaneous and relatively fast hydrogen evolution from acid solutions by these reduced forms of the heteropolyacids, without any auxiliary catalysts.

The reaction has been studied most fully for solutions of HPA-IV (silicotungstic acid),[64,66] whose structure is shown in Fig.5. It was found that HPA-IV reduced by two electrons on zinc amalgam (HPA.H_2) can evolve hydrogen rapidly from aqueous solutions in a yield of almost 100% of stoichiometric for the reaction

$$\mathrm{HPA\cdot H_2} \xrightarrow{k_{eff}} \mathrm{HPA\cdot H^{+1}/_2H_2\uparrow} \ . \qquad (4)$$

The kinetics of this process satisfy the scheme

$$\mathrm{HPA.H_2} \xrightarrow{k_1} \mathrm{HPA + H_2\ (slow\ H_2\ evolution)} \ , \qquad (4a)$$

$$\mathrm{HPA.H_2 + HPA \rightarrow 2HPA.H\ (fast\ disproportionation)} \ , \qquad (4b)$$

which corresponds to a first-order equation for the change in concentration of the reactants in the overall reaction. In this scheme HPA and HPA.H are, respectively, the initial (oxidised) form of the acid and the form reduced by two electrons (HPA-IV). The rate constant k_1, measured in three independent experiments from the disappearance of HPA.H_2 (monitored by an optical method) and from the accumulation of H_2 (monitored chromatographically) or of HPA.H (monitored by ESR), was found to be $k_1 = (3.5 \pm 2) \times 10^{-4}$ s^{-1}. (The k_1 value given here is a slight improvement over the previously reported value[64] $k_1 = k_{eff}/2 = (6 \pm 4) \times 10^{-4}$ s^{-1}.)

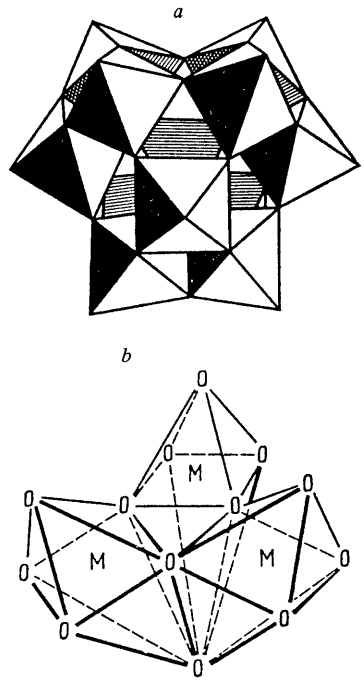


Figure 5. (*a*) Typical structure of heteropoly anions of the 12-series. The metal cations M are within the corner- and edge-sharing octahedra formed by the oxygen anions, the hetero-atom lies at the centre of the heteropoly anion; (*b*) configuration of the ions in a "triad" of adjacent octahedra.

The k_1 values obtained from the disappearance of HPA.H_2 and from the accumulation of H_2 are shown, as an example, in Fig.6. The fast disproportionation step (4b) is further confirmed by the lower yield of H_2 caused by the addition of the oxidised form to the solution, while the constant k_1 for the H_2 evolution process is unchanged.

It was found[66] that the hydrogen evolution rate constant k_1 is almost independent of pH in the range pH 1–4. This means that the protonation of the HPA forms reduced by one or two electrons cannot be rate-limiting, and we may assume that the step which controls the rate of evolution is the reduction of the strongly bound ("isolated") protons, previously observed[67] by NMR in the crystal hydrates of the reduced forms of some HPA, or the reduction of water molecules solvating the HPA.H_2 species. The mechanism of this reaction has not yet been fully investigated, but a number of significant features can already be pointed out. Thus we have found[66] a marked isotope effect, giving an almost two-fold decrease in reaction rate between ordinary water and

heavy water. The isotope effect confirms that the rate-limiting step of reaction (4) involves protons or water molecules. We also found that the reaction has a low activation energy $E^{\neq} = 6 \pm 3$ kcal mole^{-1} but a high and negative entropy of activation $\Delta S^{\neq} \cong -50$ e.u. The large value of $|\Delta S^{\neq}|$ can be explained, for example, by the complexity of the elementary act (reduction of internal protons with transfer of two electrons from the HPA.H_2 skeleton to two bound protons already in close proximity and ready to form an H_2 molecule). We also note that this reaction is markedly accelerated by visible (including red) light, which assists the transfer of electrons from the HPA.H_2 skeleton to protons or water molecules attached to the skeleton by exciting the inter-valency charge transfer levels of the reduced forms of HPA.[62,68]

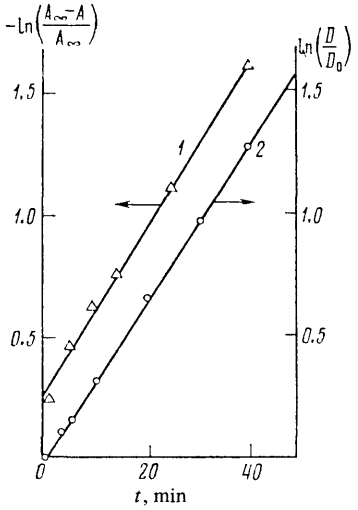


Figure 6. Kinetics of the hydrogen evolution (*1*) and of the disappearance of HPA.H_2 (*2*) in aqueous solutions of reduced 12-silicotungstic heteropolyacid (HPA-IV) at pH 2 and room temperature under anaerobic conditions: A is the height of the hydrogen peak in the chromatogram, A_∞ defines the total hydrogen evolution (initial concentration of heteropolyacid 2.2×10^{-3} M); D is the optical density of the solution at $\lambda = 650$ nm for an optical path 1 cm long, D_0 refers to the initial instant (initial concentration of heteropolyacid 5×10^{-4} M).

Hydrogen evolution has been observed also from aqueous-alcoholic solutions (0.1–10 M in alcohol) of phosphomolybdic acid reduced by six electrons (HPA-I), silicomolybdic acid reduced by four electrons (HPA-II), and phosphotungstic acid reduced by two electrons (HPA-III).[65] The rate constants ($k_1 \cong 10^{-4}$–10^{-3} s^{-1}) for all these HPA were close to the value $k_1 = (3.5 \pm 2) \times 10^{-4}$ s^{-1} given above for HPA-IV in aqueous solution. Hence we can assume that the evolution reaction has the same rate-limiting step for any highly reduced form of these heteropolyacids.

The ability of the reduced forms of HPA to evolve hydrogen from aqueous solutions, coupled with the well known tendency of HPA to be reduced by various types of reducing agents, suggest that HPA may act as homogeneous catalysts for the evolution of hydrogen from water by various reducing agents.

In fact, HPA-I and HPA-II catalyse the evolution of hydrogen from acidic aqueous solutions of several two-electron reducers, including relatively weak ones such as tin(II) ($E_0 = 0.15$ V relative to the NHE) or the sulphite ion SO_3^{2-} ($E_0 \cong 0.07$ V). We note that in the presence of these reducing agents the formation of highly reduced forms of HPA-I and HPA-II was not observed, and the rate of evolution of H_2 was much lower than the rate of evolution from highly reduced forms of HPA under otherwise similar conditions. Hence we may assume that the observed slow evolution of hydrogen (over tens of hours) is due either to the very weakly reduced forms of HPA-I and HPA-II themselves (for example, by the reaction HPA.H + HPA.H → 2HPA + H_2, which can go from left to right at low H_2 pressures) or to the disproportionation of these forms to give more highly reduced heteropolyacids, which can evolve hydrogen (as we shall show below) with fairly high rate constants.

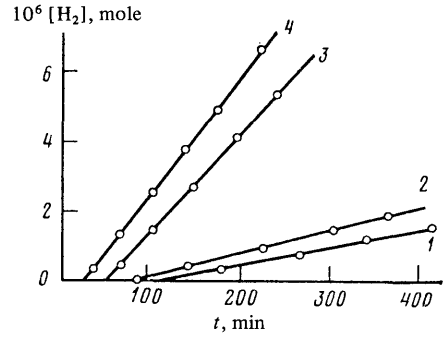


Figure 7. Kinetics of hydrogen evolution from 8 cm^3 of an 8.7 M solution of ethanol in water containing 0.25 M H_2SO_4 and: *1*) 1.3×10^{-4} M HPA-I, *2*) 10^{-4} M HPA-II, *3*) 5×10^{-4} M HPA-III, *4*) 4×10^{-4} M HPV-IV, irradiated with filtered u.v. light ($\lambda < 400$ nm) from a DRSh-1000 lamp.[65]

Heteropolyacids can also act as photocatalysts and bring about (under the influence of light) endoergic ($\Delta G > 0$) reactions in which hydrogen is evolved from water as a result of the irreversible removal of donors. Thus we have observed[65] hydrogen evolution by irradiation of oxidised forms of heteropolyacids in aqueous-ethanolic (0.1–10 M in alcohol) solutions at pH 1–4 with near u.v. light. Typical kinetic curves for this process are shown in Fig.7. We note that hydrogen evolution begins after a period of induction, and then proceeds at a constant rate. The rate of evolution stays constant even after lengthy irradiation, when the number of moles of H_2 evolved is much greater than the number of moles of HPA present in the irradiated solution.

Thus the hydrogen evolution process is truly catalytic. From the absorption spectra in the visible and u.v. regions and from fast redox titrations with $KMnO_4$ solutions we find that under the influence of light of wave length $\lambda \leq 400$ nm, HPA-I is reduced by two, four, and six electrons successively during the induction period, HPA-II by two and four electrons, and HPA-III and HPA-IV by one and two electrons. The quantum yield of the formation of reduced forms of HPA in the initial portions of the kinetic curves of Fig.7 (at $\lambda = 333$ nm) is several per cent for HPA-I and HPA-II and ~20% for HPA-III and HPA-IV.[65,69] Hence the induction

period of the H_2 evolution kinetic curves seems to be related to the accumulation of forms of HPA which are reduced sufficiently to evolve hydrogen spontaneously from acid aqueous-ethanolic solutions. These reduced forms of HPA are produced by the oxidation of ethanol. The detection[65] of acetaldehyde (in a proportion of 1 : 1 with the evolved hydrogen) after the photocatalytic reaction is consistent with this conclusion.

A decrease by a large factor in the intensity of u.v. light causes a substantial increase in the period of induction, though the rate of evolution of H_2 on the linear part of the curve is only marginally affected. The generation of hydrogen continues even after the light is switched off: we observe only a gradual slowing down as the reduced form of the HPA is used up[65].

For aqueous-ethanolic solutions of silicotungstic acid (HPA-IV) a rate constant of $k_1 \cong 5 \times 10^{-4}$ s^{-1} was calculated for the evolution of hydrogen on the stationary part of the accumulation curve (Fig.7). The constant was defined as the ratio of the rate of evolution of H_2 to the steady-state concentration of the two-electron reduced form HPA.H_2 of this heteropolyacid (see above).

These facts suggest the following overall scheme (for HPA-III and HPA-IV, say) to describe the photocatalytic evolution of H_2 from aqueous-ethanolic solutions of the oxidised forms of heteropolyacids:

$$C_2H_5OH + HPA \xrightarrow{h\nu} CH_3CHO + HPA \cdot H_2 \qquad (5a)$$

$$HPA \cdot H_2 \longrightarrow HPA + H_2\uparrow \cdot \qquad (5b)$$

The rate-limiting step is reaction (5b), which takes place spontaneously even in the absence of light but (as was pointed out above) can be accelerated by irradiation with visible light of wavelength corresponding to the intervalency charge transfer absorption band. Unlike reaction (5b), reaction (5a) proceeds only under irradiation. It is almost certainly a complex reaction, i.e. a reaction consisting of several steps[69]. Further work is needed to clarify the relative roles of two-electron processes

$$C_2H_5OH + HPA \xrightarrow{h\nu} CH_3CHO + HPA \cdot H_2$$

and of one-electron processes

$$C_2H_5OH + HPA \xrightarrow{h\nu} CH_3\dot{C}HOH + HPA{\cdot}H$$

$$C_2H_5OH + HPA{\cdot}H \xrightarrow{h\nu} CH_3\dot{C}HOH + HPA \cdot H_2$$

$$CH_3\dot{C}HOH + HPA \rightarrow CH_3CHO + HPA{\cdot}H$$

$$CH_3\dot{C}HOH + HPA{\cdot}H \rightarrow CH_3CHO + HPA{\cdot}H_2,\ HPA + HPA{\cdot}H_2 \rightleftarrows 2HPA{\cdot}H$$

in reaction (5a).

Thus in this photochemical process the heteropolyacids take part in cyclic reactions including steps in which the HPA are reduced by two or more electrons, followed by hydrogen evolution by the reduced forms of HPA and by regeneration of the initial (oxidised) forms. Under these conditions the HPA performs two functions at the same time: that of a photo-catalyst and that of a catalyst for the "dark" H_2 evolution reaction. The photo-catalytic hydrogen evolution

$$C_2H_5OH \xrightarrow[PC]{h\nu} CH_3CHO + H_2\uparrow$$

in this system is an endoergic process, leading to a small (~0.2 eV) acquisition of energy from the light at each act of evolution of molecular H_2.

III. EVOLUTION OF OXYGEN FROM WATER

This step is much more difficult than the hydrogen evolution to carry out in practice, because reaction (2) requires the transfer of four electrons, and furthermore conditions leading to the formation of the product molecule (oxygen) in the triplet rather than the singlet state must be provided. A systematic search for catalysts for reaction (2) has only recently been started. We have examined[70–73] a series of homogeneous metal complex catalysts for reaction (2), using the compounds $Ru(bipy)_3^{3+}$, $Fe(bipy)_3^{3+}$, and $Fe(phen)_3^{3+}$ as the oxidiser D^+. Some of these catalysts allow oxygen evolution from water not only in alkaline or neutral solutions but also in weakly acid solutions (down to pH 5). The series of homogeneous catalysts for the oxygen evolution step was also reported from another laboratory almost simultaneously[74–77]. Many heterogeneous catalysts for this step have also been discovered[21,52,75–87]: for example, the oxides of ruthenium, platinum, iridium, cobalt, and manganese.

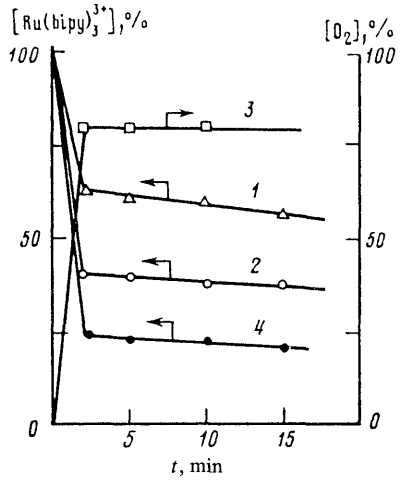


Figure 8. Kinetics of the reduction of the oxidiser and of the formation of oxygen during fast adjustment to a more alkaline pH of 8×10^{-4} M solutions of $Ru(bipy)_3^{3+}$ in 0.01 *N* HCl: *1*) and *4*) adjusted to a final pH of 3.5 and 6 respectively in the absence of the catalyst, *2*) and *3*) adjusted to a final pH of 3.5 in the presence of the catalyst (5×10^{-5} M $CoCl_2$), temperature 298 K. The stoichiometry of the oxygen evolution was calculated with respect to the reduced fraction of the oxidiser[73].

1. Systems with Homogeneous Catalysts Based on Transition Metal Complexes

We have studied two classes of compounds which act as homogeneous catalysts for reaction (2): 1) the partially hydrolysable (or aquated) complexes of various transition metals with nitrogen- or oxygen-containing ligands[70,71,73] (see also Ref. 76), and 2) water-soluble phthalocyanines and porphyrins of various metals[72]. Catalysts of the first type are the more effective, the highest activity (up to one molecule of O_2 per metal atom in the catalyst per minute at 20 °C) being found in the iron, cobalt, and copper complexes, but they are less stable than the catalysts of the second type.

It has been reported[75–77,79,84] that compounds of the first type have a high catalytic activity not only for the "dark" evolution of oxygen from water but also in model photo-catalytic systems, in which the evolution of oxygen from water is coupled with the irreversible reduction of an electron acceptor.

The study of the mechanisms by which the homogeneous catalysts contribute to reaction (2) is still in progress, but some important features of their mode of action have already been established. We should stress first of all the experimental difficulties encountered in the study of reaction (2). When complexes with bipy or phen are used as the oxidiser D^+ the reaction is very sensitive to effects of the wall of the vessel. For example, in glass reactors oxygen is sometimes evolved by reaction (2) even in the absence of special catalysts, the amount of oxygen evolved depending on the composition of the glass and on the presence of rough areas or micro-cracks on its surface. The requirement of wall inertness is most fully met by polyethylene vessels.

Another difficulty in the study of the mechanism of action of these catalysts in reaction (2) is the lack of sufficiently fast methods of recording the kinetics of oxygen evolution. The characteristic times of the fast step in reaction (2) in the presence of the catalyst and after pH adjustment to the required alkalinity are usually a few seconds (see below, and Fig.8). However, the time constant of the fastest instrumental methods of detecting oxygen directly in solution (by using a Clark electrode) is 20–30 s. Therefore the most informative data on the kinetics of oxygen evolution (i.e. directly from the activity of the catalyst) are not available to us at the moment. The effectivness of the catalyst can only be characterised by the ratio of the amount of oxygen evolved to the amount expected from stoichiometry considerations. This ratio (β), expressed in per cent, will be termed the effectiveness of the catalyst.

It is found that 100% effectivness is only very rarely achieved in a catalyst: a much lower β value is usually obtained. This is probably due to the partial loss of oxidiser (D^+) by fast oxidation side-reactions involving the ligands (which enter into the composition of both the oxidisers and the catalysts). We note that side reactions in the absence of the catalyst can cause substantial reduction of D^+ in less than 10 s (~40% in acid solutions and ~90–95% in alkaline solutions, see below and Fig.8): no oxygen is evolved in this case. Thus the role of the catalyst in reaction (2) is to guide the reduction of D^+ towards the evolution of oxygen rather than towards the oxidation of the ligands.

In the presence of catalysts, after adding alkali to obtain the required pH to the acid (pH 1–2) solutions containing the initial reagents (oxidiser and catalyst) as in the experiments[70–72] on the initiation of the oxygen evolution, only a part of the oxidiser is consumed in the fast (a few seconds) oxygen evolution and ligand oxidation processes (see Fig.8). The unused oxidiser D^+ is reduced more slowly, in times of the order of tens of minutes. With some (but not all) catalysts this slow reduction of the oxidiser is accompanied by evolution of oxygen from the water by reaction (2).

The loss of oxidiser in the fast step of the process is strongly dependent on the pH of the solution. Thus if alkali is added to give pH 3 approximately one-half of the oxidiser is usually reduced rapidly; at pH 9 this loss amounts to 80–90%.

It is interesting to find that the effectiveness β measured at pH 3 for most of the homogeneous catalysts under the most favourable conditions and referred to the amount of oxidiser reduced in the fast reactions does not vary over a wide range (see Table 2). We should also note the complex behaviour of some of these homogeneous catalysts in solutions with different pH. Thus, whereas at pH 3 all the cobalt complexes have approximately the same effectiveness as catalysts when $Ru(bipy)_3^{3+}$ is used as the oxidiser (see Table 2), in solutions of pH 9–10 they can be arranged in the following series of increasing effectiveness:

$$\underset{\beta,\ \%}{\text{Catalyst}}\ \underset{10}{Co(NH_3)_6^{3+}} < \underset{39}{Co(NH_3)_5Cl^{2+}} < \underset{42}{Co(NH_3)_5(H_2O)^{3+}} < \underset{60}{Co^{2+}(aq)} < \underset{66}{Co(NH_3)_4(H_2O)_2^{3+}} < \underset{70}{Co(bipy)_{3-x}(H_2O)_x^{3+}}$$

This series probably reflects the role of the coordination of water molecules or hydroxyl ions to the catalyst molecules in the evolution of oxygen molecules under these conditions.

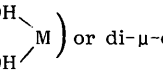
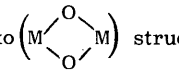
Table 2. Consumption of oxidiser (Q) in the fast step of the water oxidation process and effectiveness β of various homogeneous catalysts in an 8×10^{-4} M solution of $Ru(bipy)_3^{3+}$ after pH adjustment to pH 3.0–3.2 at 298 K (c is the concentration of catalyst) [73].

$10^4 c$, M	Q, %	β, %	$10^4 c$, M	Q, %	β, %
0	40	0	$[Co(NH_3)_5(H_2O)]Cl_3$		
$CoCl_2$			0.9	30	45
0.5	60	85	8.3	55	85
2.2	55	75	30.0	55	85
4.3	30	65	$[Co(NH_3)_4(H_2O)_2]Cl_3$		
6.4	20	27	2.0	50	70
Cis- and *trans*-$[Co(en)_2Cl_2]Cl$, *trans*-$[Co(en)_2Cl(H_2O)]Cl_2$			20.0	40	70
0.5	60	80	Tetrasulphophthalocyanine of cobalt(II)		
2.2	60	75	0.07	55	70
8.3	60	75	0.22	60	60
20.0	45	70	0.64	65	40
$[Co(NH_3)_5Cl]Cl_2$			$[(bipy)_2FeOFe(bipy)_2]Cl_4$		
5.0	50	80	0.25	60	85
10.0	50	80	1.0	60	85
			10.0	50	90

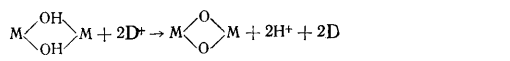
Note. The precision of the determination of Q and β is ±5%.

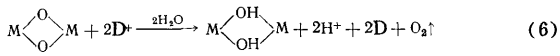
The complexity of the homogeneous catalysis process combining the above catalysts with *tris*-bipyridyl and *tris*-phenanthroline complexes as oxidisers is confirmed by the strong dependence of β on the experimental conditions, in particular the pH and the storage time of the solutions before the reaction, and also on the procedure used in mixing the reagents (for example, whether the catalyst is added to the acid solution of oxidiser before adding alkali, or whether the catalyst is added in an already alkaline solution to an acid solution of the oxidiser). Evidently these results can be explained by postulating hydrolysis processes in the activation of the catalyst: of course, both the rate and the direction of these processes can be expected to depend on the pH of the medium.

The role of hydrolysis in the conversion of the initial complexes into catalytically active compounds has been demonstrated for systems containing the complexes $Fe_m(bipy)_n \cdot (OH)_p^{(3m-p)+}$ or $Fe_m(phen)_n(OH)_p^{(3m-p)+}$ at pH > 4 as catalysts[70]. It was shown that the bipyridyl and phenanthroline complexes of iron(III) containing OH^- ions as ligands are much more effective catalysts than the same complexes without the OH^- ligands. By comparing the data on the

effectiveness of these complexes with the data on their hydrolysis mechanism we conclude that in some of our systems the catalytically active intermediates are binuclear di-μ-hydroxo  or di-μ-oxo  structures (where M is a metal).

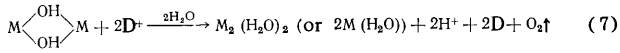
Evidently, the oxygen evolution reaction begins with a series of four consecutive one-electron reactions in which the catalyst is oxidised by D^+ particles, and each metal ion in the binuclear catalyst can give up two electrons to the oxidisers. The subsequent reactions (oxygen evolution and regeneration of the active forms of the catalyst) proceed without the formation of free (non-coordinated) forms of intermediates in the oxidation of water such as $\dot{O}H$ radicals and also, at least for some of the present catalysts, H_2O_2 molecules and $H\dot{O}_2$ radicals[70]. For example, the catalytic action of partially hydrolysed bipyridyl complexes of iron(III) can be interpreted by the following alternative schemes:



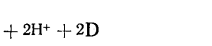


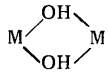
(6)

or



(7)



For the catalysts in which M = Fe(III) or Co(III) the evolution of molecular oxygen from an oxidised  centre can take place through the formation and dissociation of a binuclear μ-peroxo complex

$$M-O_2^{2-}-M \rightleftarrows 2M^- + O_2\uparrow$$

or a mononuclear peroxo complex

$$M-O_2^- \rightleftarrows M-O_2 \rightleftarrows M^- + O_2\uparrow$$

as intermediates. These reversible oxygenation reactions of cobalt(II) and iron(II) complexes in alkaline solutions are well known (see, for example, Refs.88–91).

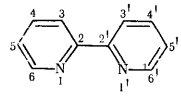
Among the catalysts of the second type the most effective (β ≅ 70%) are the tetrasulphophthalocyanine and tetrasulphophenylporphin of cobalt(II).[72] If $Ru(bipy)_3^{3+}$ is used as the oxidiser D^+ the effectiveness of the tetrasulphophthalocyanines of various metals at pH 9 can be arranged in the following sequence:

Metals	Co(II)	> Fe(II)	> Zn II	> Cu(II)	> Ni(II)	> Mn(II)	> Cr(II)
β, %	65	47	25	21	18	14	5

Metal-free phthalocyanines do not show a significant catalytic activity. The mechanism of the action of these catalysts is still unclear. We can note, nevertheless, that the catalytic activity of metal phthalocyanines is not produced by dissociation with formation of aquo-complexes of the metal ions. Thus, at ~10^{-5} M concentration the aquo-ions of Cr(III), Mn(II), Bi(II), and Al(III) have no catalytic activity towards the oxidation of water by oxidisers of the $Ru(bipy)_3^{3+}$ type, whereas the phthalocyanines of the same metals at the same concentration have a marked catalytic activity[72]. We should also stress that in very acid solutions (in which the reaction (2) is suppressed) some of these metal phthalocyanines undergo a fast and quantitative two-electron oxidation accompanied by one-electron reduction of the oxidiser $Ru(bipy)_3^{3+}$. It is at least possible that in more alkaline solutions these doubly oxidised forms of metal phthalocyanines take part (as intermediates) in the oxygen evolution reaction.

An interesting feature of these catalysts, providing additional evidence of the complexity of the catalytic reaction (2), is the presence at pH > 4 of clear maxima in the plots of the effectiveness of the catalyst against concentration. For example, at pH 9 the optimum concentration for catalysts of the first group is ~10^{-4} M, and for catalysts of the second group ~10^{-5} M. The existence of optimum concentrations of the homogeneous catalysts is noted also for the evolution of oxygen at pH 3 (see Table 2), but in this case the dependence of β on the concentration of the catalyst is usually monotonic, without extrema.

The possibility that the role of the oxidisers D^+ in reaction (2) goes beyond the transfer of an electron from the catalyst to the oxidiser cannot be excluded. Indeed, the addition of anions (chloride, perchlorate, sulphate, carbonate, acetate, borate, etc.) as sodium salts partially suppresses both the evolution of oxygen in reaction (2) and the secondary reduction of D^+ by the oxidation of the ligands (even in the absence of catalysts). However, the catalyst effectiveness β calculated from the amount of oxidiser D^+ which is reduced does not vary significantly under these conditions. We are therefore forced to the conclusion that reaction (2) and the secondary reaction share a number of steps which are affected by the interaction between the particular oxidised (D^+) used in these experiments and the anions, but are unaffected by the catalyst. Thus, in the proton magnetic resonance spectra of the complex $Ru(bipy)_3^{3+}$ a strong chemical shift of the signals from the 6 and 6′ protons of bipyridyl



is observed after addition of various anions (see Fig.9), due no doubt to the out-of-sphere coordination of the anions to the bipyridyl ligand. This anion coordination may also suppress some other interaction of the oxidiser with water molecules (or their ionic forms) playing an as yet unrecognised role in both reaction (2) and the secondary process. Work on these effects is in progress.

At the same time the inner-sphere coordination of water to the cation of the oxidiser by replacing even one of the coordinating nitrogen atoms of the ligands does not appear to be an intermediate step of reaction (2). Thus we have shown[73] that the mixed complexes of ruthenium(III) $[Ru(bipy)_2(Py)_2]^{3+}$ (where Py is pyridine), in which the replacement of the ligands probably occurs at different rates and with different equilibrium constants than for the *tris*-bipyridyl complex, can evolve oxygen from water with the same effectiveness as $Ru(bipy)_3^{3+}$ when used as the oxidiser D^+ in the presence of homogeneous catalysts[73]. However, in the complexes $[Ru(bipy)_2.(Py)(H_2O)]^{3+}$, which contain water in the first coordination sphere, this property is not found because their oxidation potential is too low. We note that the even more highly hydrolysed form of this complex $[RuO(bipy)_2]^{2+}$, though itself unable to oxidise water, is nevertheless an effective homogeneous catalyst for the oxidation of water when $Ru(bipy)_3^{3+}$ is used as the oxidiser D^+ [73] (see also Refs. 92 and 93).

We may hope that work now in progress on the mechanism of the homogeneous catalysis of reaction (2) by using $Ru(bipy)_3^{3+}$ as the oxidiser will lead to the development of effective and stable catalysts for the oxygen evolution step, able to operate in a closed water decomposition cycle using the $Ru(bipy)_3^{2+}$ comples as the photocatalyst for step (1).

2. Systems with Heterogeneous Catalysts Based on the Hydroxides and Mixed Oxides of the Transition Metals

The search for and study of potential heterogeneous (as well as homogeneous) catalysts for reaction (2) is an important current problem. As was mentioned above, these catalysts are being studied in a number of laboratories, the materials in most cases being simple oxides. We have examined[94] the possibility of using another class of compounds as heterogeneous catalysts of reaction (2): base metal hydroxides and spinels, which are mixed oxides of general formula $M^{II}M^{III}_2O_4$ (where M^{II} and M^{III} are bivalent and a tervalent metal respectively). Spinels of various compositions are widely used as oxidation catalysts and as anodes for the electrochemical evolution of oxygen[95].

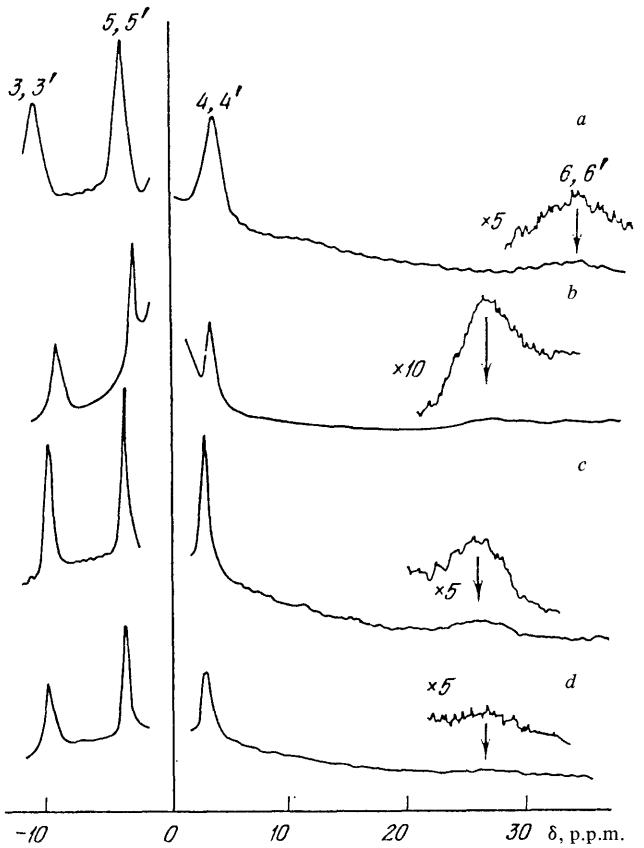


Figure 9. NMR spectra ("Bruker CXP-300" Fourier spectrometer, frequency 300 MHz) of a 10^{-3} M solution of $Ru(bipy)_3^{3+}$ in D_2O containing also: (*a*) 0.01 M DCl, (*b*) 1 M DCl, (*c*) 1 M NaCl, (*d*) 1 M Na_2SO_4; temperature 293 K, 200 spectral scans. The chemical shifts are measured relative to the signals of the water protons. The peaks are numbered according to the position of the protons in 2,2′-bipyridyl.

Measurements of the effectiveness β of heterogeneous catalysts (hydroxides and spinels) used in conjunction with *tris*-bipyridyl complexes of ruthenium(III) and iron(III) as the oxidiser D^+ are summarised in Table 3. As in the study of the homogeneous catalysts, the amount of oxygen evolved was determined after adding a 0.1 *N* solution of NaOH to weakly acid (pH ~ 2, spinels) or to neutral solutions (hydroxides) of the oxidiser containing the catalyst. The weight of catalyst added was 20 mg for 10 ml of solution; no oxygen was evolved unless the solution was made alkaline.

We should stress that spinels prepared by standard methods may contain various impurities such as the salts used in their preparation or oxides or hydroxides foreign to the spinel. Most of these impurities are removed by steeping the spinel in a weakly acid solution, but this treatment transfers to the solution metal ions which can act (as stated above) as homogeneous catalysts for reaction (2) even at very low concentrations (10^{-4}–10^{-5} M). Therefore all the spinel samples were finely ground before the determination of β and washed repeatedly with 0.1 *N* hydrochloric acid until free from metal ions, thus ensuring the absence of effects from homogeneous side-reaction on the measurements.

Table 3. Effectiveness β of heterogeneous catalysts in 8×10^{-4} M solutions of $Ru(bipy)_3^{3+}$ and $Fe(bipy)_3^{3+}$ at 298 K.

Catalyst	β %	Catalyst	β %
Oxidiser $Fe(bipy)_3^{3+}$		Oxidiser $Ru(bipy)_3^{3+}$	
$NiCo_2O_4 \cdot Co_3O_4$	70	$CoFe_2O_4$	60
$CuCr_2O_4 \cdot CoCr_2O_4$	50	$CoFe_2O_4$*	60
$CoFe_2O_4$	40	$CoFe_2O_4$**	17
$FeCr_2O_4$	40	$Co^{II}Co_2^{III}O_4$	35
$Co^{II}Co_2^{III}O_4$	37	$Cr(OH)_3$	60
$CoCr_2O_4$	35	$Cu(OH)_2$	45
		$Fe(OH)_3$	40
		$Co(OH)_3$	25
		$Ni(OH)_3$	20
		$Al(OH)_3$	0

*pH 5–6; **pH 3–4, otherwise pH 10–11.

Note. The precision of the measurement of β is ±5%. The catalyst was ground to a powder of particle size less than 0.05 mm and was taken in amounts of 20 mg per 10 cm^3 of solution.

The catalytic activity of the iron(III) and cobalt(III) hydroxides in reaction (2) is mentioned also in Ref. 76.

The heterogeneous catalysts studied in our laboratory are similar to the homogeneous catalysts in effectiveness (see Tables 2 and 3), but their stability is much higher. In addition to the substances listed in Table 3, zinc and copper ferrites and iron and copper cobaltites have been found to be catalytically active in reaction (2).

It would be premature to attempt a discussion of the mechanism of the oxidation of water by reaction (2) in the presence of spinels. In particular, the effect of the spinel structure and of the nature of the bivalent and tervalent metal cations is still unclear. It is obvious, however, that surface compounds containing water or its fragments must play an important part in reaction (2). In contact with water the spinel surface may become rapdily hydroxylated, so that the catalytically active centres are not the spinels themselves but compounds not very different from the hydroxides of the corresponding metals. In this case we would expect the formation on the catalyst surface of bridging compounds similar to the complexes proposed for reactions (6) and (7).

IV. PHOTOCHEMICAL CHARGE SEPARATION

The lack of effective methods of realising reaction (2) in practice is the most serious obstacle to the development of molecular photocatalytic systems for the decomposition of water in a closed cycle (i.e. a cycle in which no substance is consumed irreversibly except water). The main problem is to suppress the reverse recombination reaction $D^+ + A^- \rightarrow D + A$, which is a simple exothermic process and therefore usually much faster than the complex catalytic reactions (2) and (3).

Several possible ways of suppressing the reverse reaction are being studied in our laboratory at present. Two of these will be discussed below: one based on the use of lipid vesicles, the other on micro-emulsions.

1. Charge Separation in Solutions of Lipid Vesicles

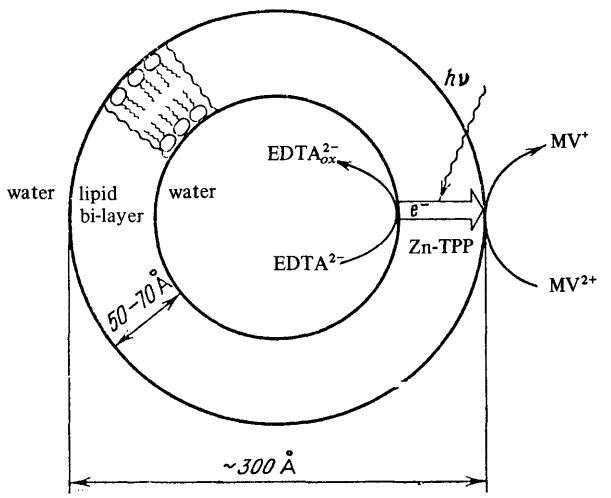


Figure 10. Scheme of the photo-transfer of an electron through the membranes of lipid vesicles containing Zn-TPP as photocatalyst.

The vesicles, whose structure is shown schematically in Fig.10, consist of a shell formed by a two-layer lipid membrane. The vesicles described below were prepared by using either the natural lipid lecithin or the synthetic lipid dipalmitoylphosphatidylcholine (DPPC). The inner cavity of the vesicles was filled with an aqueous solution of electron donors (the sodium salt of ethylenediaminetetra-acetic acid, Na-EDTA, or nicotinamide dinucleotide, NADN), whereas the outer volume contained an electron acceptor (methylviologen, MV^{2+}). It has been convincingly shown[81,96-99] that irradiation of solutions of vesicles containing photo-catalysts in the membrane can produce electron transfer across the membrane, leading to the formation of D^+ and A^- species which are prevented from recombining by being on opposite sides of the membrane. The photocatalysts used in these experiments had long hydrophobic groups: chlorophyll[97,100], or surface-active derivatives of zinc porphyrin[98] or of the *tris*-bipyridyl ruthenium complex[81,96,99]. The photo-catalyst used in our work was much simpler, and did not contain long hydrophobic groups: zinc tetraphenylporphin (Zn-TPP).[101-104]

Irradiation of a solution of vesicles with light of wavelength corresponding to the Soret band of Zn-TPP ($\lambda \cong 425$ nm) or to its long-wave absorption bands ($\lambda > 500$ nm) causes photo-transfer of electrons from the donor particles within the vesicle to acceptor particles outside it (see Fig.11), the metallo porphyrin contributing repeatedly to the cycle in which MV^{2+} is reduced by the electron donors and thus behaving as a true photocatalyst[101]. The quantum yield of the reduction of MV^{2+} in the natural lecithin system irradiation with focussed filtered light from a DKSSh-1000 lamp in the region of the Soret band or of the long-wave absorption bands was 0.01 to 0.1%, the highest observed quantum yield (for light in the long-wavelength absorption band region) being $0.15 \pm 0.04\%$.[104]

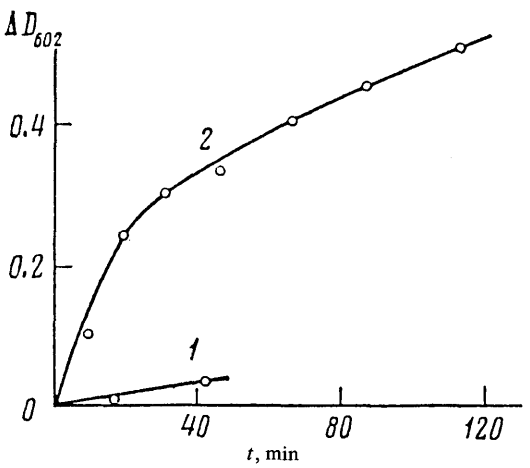


Figure 11. Change in optical density at $\lambda = 602$ nm due to the accumulation of MV^+ during irradiation by light with $\lambda > 500$ nm (from a DRSh-1000 lamp) of a solution of egg lecithin vesicles containing Zn-TPP: curve *1* was obtained in the absence of electron donors, curve *2* in the presence of 0.2 M Na_2-EDTA inside the vesicles[101]. The concentration of lecithin, Zn-TPP, and MV^{2+} are (respectively) 2.4×10^{-3} g cm^{-3}, 6×10^{-5} M, and 2×10^{-2} M; temperature 298 K. When a synthetic lipid was used the accumulation of MV^+ in the absence of Na_2-EDTA was negligible.

The observation of electron photo-transfer across a membrane by light of wavelength corresponding to the long-wave absorption bands, i.e. under the influence of quanta able to excit only the first singlet level of Zn-TPP, is evidence of the important part played by the lower excited states of Zn-TPP in the electron photo-transfer process.

In the flash photolysis of a solution of vesicles containing only Zn-TPP but no electron donors or acceptors the transient optical spectrum shows an absorption assigned to the triplet electronically excited state of porphyrin ($Zn\text{-}TPP^T$) and to the porphyrin cation radical ($Zn\text{-}TPP^+$). The very fast deactivation of the triplet states is probably caused by the annihilation reaction

$$2Zn\text{-}TPP^T \longrightarrow 2Zn\text{-}TPP + \Delta E \qquad (8)$$

The rate of this process is much higher in the vesicle solution than in a homogeneous solution containing the same total amount of porphyrin because of the high local concentration of porphyrin in the lipid bi-layer (up to 2.5×10^{-2} M, i.e. well in excess of the average concentration). The cation radical Zn-TPP^{+} may also be produced by the annihilation of triplet states:

$$2\text{Zn-TPP}^{T} \rightarrow \text{Zn-TPP}^{+} + \text{Zn-TPP}^{-} . \qquad (9)$$

Unfortunately we were unable to detect the anion radical Zn-TPP^{-} directly because of the strong absorption of the triplet states in the region of the characteristic absorption lines of Zn-TPP^{-}.

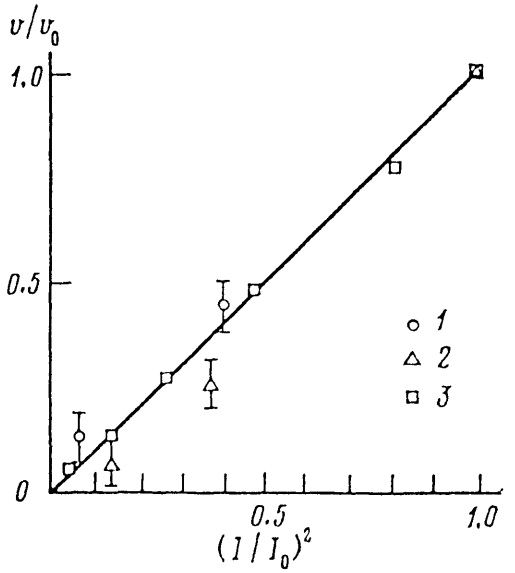


Figure 12. Initial rate (v) of accumulation of MV^{+} in a solution of lipid vesicles against the intensity (I) of exciting light for irradiation in the region of the Soret band (*1*, *3*) and of the long-wave absorption bands (*2*) of zinc porphin: *1*) and *2*) refer to vesicles of natural lecithin, under the conditions stated in Fig.11, *3*) refers to vesicles of synthetic DPPC, with concentrations of DPPC and MV^{2+} of 5×10^{-3} g cm^{-3} and 0.1 M respectively, [Zn-TPP] : : [DPPC] = 1 : 50, other conditions as in Fig.11;[101,102] v_0 is the initial rate of accumulation of MV^{+} for a light intensity I_0.

When MV^{2+} is present outside the vesicles a strong and long-lived absorption due to the cation radicals MV^{+} and Zn-TPP^{+} is observed immediately after the flash. The disappearance (by recombination) of these products of the flash photolysis takes place in parallel, and is described by a second-order equation with rate constant $k = (1.9 \pm 0.2) \times 10^{8}$ litre mole^{-1} s^{-1}. In this way the concentrations of MV^{+} and Zn-TPP^{+} immediately after a flash $\leq 10^{-5}$ s long are about one-quarter of the concentration of Zn-TPP in the sample, i.e. they are much higher than the concentration of Zn-TPP^{+} observed immediately after the same flash but in the absence of MV^{2+}. The large amount of MV^{+} formed and its disappearance by a second-order reaction (i.e. by interaction with extraneous cation radicals rather than with the cation radicals of the matrix Zn-TPP^{+}) suggest that both the formation of MV^{+} and its migration from the reaction cage after the electron photo-transfer act have a high probability.

The presence of EDTA^{2-} as the sodium salt inside the vesicle has no effect on the flash photolysis of vesicles containing Zn-TPP, both in the presence and in the absence of MV^{2+} in the outer solution.

The one-quantum[81,96,97] and the two-quantum[98] mechanisms for the activation of photo-transfer through the membranes of lipid vesicles have been discussed in published papers. For both the natural and the synthetic lipid (at 287–333 K) we have observed[103] a square-law dependence of the initial rate of accumulation of MV^{+} on the intensity of the exciting light (Fig.12), which suggests a two-quantum mechanism for the photo-transfer involving Zn-TPP over the whole range of temperature. This dependence is observed with light of wavelength in the region of both the Soret band and the long-wave absorption bands of Zn-TPP, and therefore it is not related to the nature of the primary singlet-excited state. This suggests that the photo-transfer process involves the triplet-excited Zn-TPP molecules. It is interesting to note that when EDTA^{2-} is present on the same side (the outside) as MV^{2+}, i.e. when the membrane is used merely as a carrier of the water-insoluble photocatalyst Zn-TPP, the initial rate of accumulation of MV^{+} is linearly dependent on the light intensity, denoting a one-quantum mechanism for the photo-transfer of an electron from EDTA^{2-} to MV^{2+}.

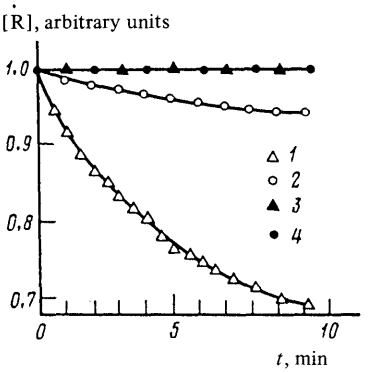
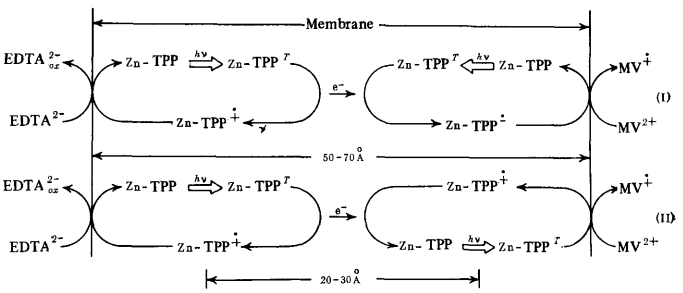


Figure 13. Kinetics of the photo-reduction of Doksil spin probes (Ṙ) trapped in vesicles of synthetic DPPC with (*1*, *2*) and without (*3*, *4*) zinc porphin in the bi-layer. Concentrations of the lipid and of Na_2-EDTA 10 mg cm^{-2} and 0.2 M respectively, [Zn-TPP] : [DPPC] = 1 : 50, [spin probe] : [lipid] = 1 : 200, 298 K. Spin probes: *1*) and *3*) 5-DOKSIL, *2*) and *4*) 16-DOKSIL.[102]

In order to determine the mechanism of electron photo-transfer through the membrane we need to establish the location of the electronically excited porphyrin molecules within the lipid bi-layer, since in principle they could be evenly distributed throughout the thickness, localised near the centre, or localised near the surface. We tried to answer this question by studying the irreversible photo-reduction of amphiphilic Doksil spin probes (a stearic acid derivative) localised in the vesicle membrane, interacting with electronically excited Zn-TPP molecules[102]. We found that under comparable conditions the rate of photo-reduction of the spin probes having an ṄO fragment near the surface of the

bi-layer (i.e. those with a paramagnetic substituent on the fifth carbon atom from the carboxyl group, "5-Doksil") is much greater than the rate of reduction of the probes with the $\dot{N}$–O fragment deep within the bi-layer (with their paramagnetic substituent on the 16th carbon atom, "16-Doksil") (see Fig. 13). Since the rate of photo-reduction of the $\dot{N}$–O fragments must increase with decreasing distance to the electronically excited Zn-TPP molecule we may conclude that the latter is preferentially localised near the surface of the bi-layer.

From these results we may suggest two alternative schemes for the phototransfer of an electron through the membrane which are consistent with both the steady-state and the flash photolysis data:



(where the symbol $EDTA^{2-}_{ox}$ refers, as before, to the products of the irreversible oxidation of $EDTA^{2-}$). According to scheme (I) the process responsible for the electron transfer through the membrane are the annhiliation of two Zn-TPP^T molecules with formation of Zn-TPP$^+$ and Zn-TPP$^-$ and the subsequent reactions of these ion radicals with $EDTA^{2-}$ and MV^{2+}. According to scheme (II) the electron transfer through the membrane is due to the reaction between Zn-TPP^T and MV^{2+}, followed by the transfer of an electron to the Zn-TPP$^+$ formed near the outer surface of the vesicle from another Zn-TPP^T particle near the inner surface, and lastly by the interaction of the resulting Zn-TPP$^+$ and $EDTA^{2-}$ particles. In both cases a square-law dependence of the initial rate of accumulation of MV^+ on the light intensity can be expected.

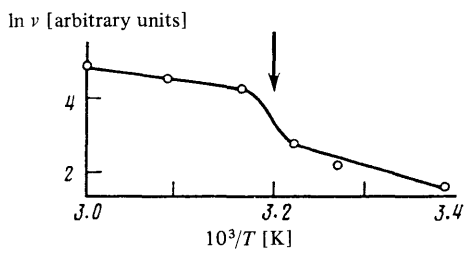


Figure 14. Temperature dependence of the initial rate (v) of accumulation of MV^+ in a solution of synthetic DPPC vesicles. Concentrations of lipid, Zn-TPP, and MV^{2+} 1.5×10^{-3} g cm^{-3}, 3.7×10^{-5} M, and 2×10^{-2} M respectively; concentration of Na_2-EDTA in the cavity of the vesicles 0.2 M. Irradiation with light in the region of the long-wave absorption bands of Zn-TPP. The arrow denotes the temperature of the phase transition of the lipid (~315 K).[103]

The published values[105] of the redox potentials of the species involved in these schemes suggest that both variants are thermodynamically possible.

As was shown above, the presence of MV^{2+} outside the vesicles causes a large increase in the initial concentration of Zn-TPP$^+$ during flash photolysis. This means that the transfer of an electron from Zn-TPP^T to MV^{2+} (on the outer surface of the vesicle) is a more effective channel for the disappearance of Zn-TPP^T than reaction (9) under the present conditions. Therefore we consider scheme (II) to be the more realistic. The diffusion of a charged photolysis intermediate (Zn-TPP$^+$) in the non-polar lipid membrane is probably slow. Under these conditions electron transfer through the membrane can occur, for example, by a tunnelling exchange between Zn-TPP and Zn-TPP$^+$. It is interesting to note that when the temperature is lowered through the melting point of the lipid the rate of photo-transfer of electrons through the membrane drops sharply but does not fall to zero (Fig. 14).[103] A similar effect (electron transfer at a significant rate below the freezing point of the system) had been observed earlier for the recombination of light-separated charges in the photo-system I of plants (see, for example, Ref. 106, and also Ref. 107 and its list of references).

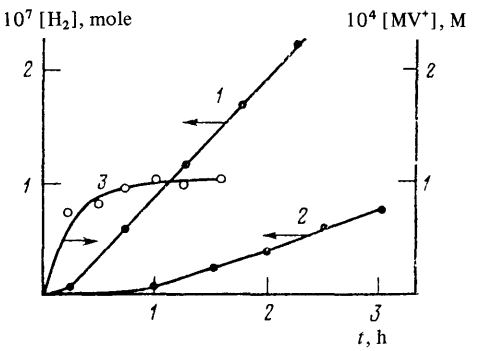


Figure 15. Kinetics of the accumulation of hydrogen over 1 cm^3 of a solution of egg licithin lipid vesicles containing Zn-TPP in the lipid bi-layer, a 0.2 M solution of Na_2-EDTA in the vesicle cavities, and in the outer volume MV^{2+} and a hydrogen evolution catalyst (*1*, *Tiocapsa roseopersicina* hydrogenase; *2*, activated Rh–AN-221 heterogeneous catalyst). Irradiation with light of $\lambda > 510$ nm from a DKSSH-1000 lamp; concentration of lipid, Zn-TPP, and MV^{2+} 6.7 mg cm^{-3}, 1.7×10^{-4} M, and 4.3×10^{-3} M respectively; temperature 303 K. Curve *3* shows the development of a steady-state concentration of MV^+ in the presence of hydrogenase (measured in parallel with the kinetic curve *1*). A pH of 7.2 was maintained both within and outside the vesicles by an ammonium buffer[104].

The continuing square-law dependence of the rate of photo-transfer of electrons through the membrane on the light intensity below the phase transition temperature of the lipid suggests that the mechanisms are similar at temperatures above and below the phase transition. The stepwise change in rate at the transition point is probably due to the unfreezing of the lateral diffusion modes of the reactants caused by the melting of the lipid. We note that a similar (stepwise) change in rate with temperature is found by flash photolysis in this system even for long-range interactions such as the triplet–triplet deactivation of excited porphyrin molecules [reaction (8)].[103]

The similarity between the mechanism of charge photo-separation by scheme (II) and the mechanism of charge photo-separation now generally accepted ("Z-scheme") for photosynthesis in plants is unmistakable. The vesicles containing metallo-porphyrins can therefore be treated as analogues of biological charge photo-separation systems, and a substantial increase in quantum yield may therefore be expected (by analogy with those systems) by suitable choice of photocatalyst, electron donor and acceptor, and lipid.

The photo-reduction of MV^{2+} by the electron donors $EDTA^{2-}$ or NADN is endothermic, and therefore (with NADN, for example) each act of photo-transfer is accompanied by the storage of 0.12 eV of energy. For irradiation with light of wavelength in the region of the long-wave absorption bands of Zn-TPP this corresponding to a storage of ~3% of the combined energy of the two light quanta needed for the photo-transfer of an electron.

Thus by inserting a fairly simple photocatalyst (zinc tetraphenylporphin) into the lipid membrane we can induce electron photo-transfer through the membrane by visible light (admittedly, so far, in low quantum yield). The reduced form of the electron acceptor used in our experiments, MV^{+}, can evolve molecular hydrogen from water even at neutral pH values in the presence of suitable catalysts. We were able to observe this process (at pH ~ 7) by adding to the solution outside the vesicles the hydrogenase enzyme *Thiocapsa roseopersicina* at ~10^{-6} M concentration, or the heterogeneous catalyst Rh–AN-221 (described above) in an activated form[104]. The effective quantum yield of the photo-catalytic hydrogen evolution measured in the stationary region (Fig.15) was $(1.0 \pm 0.3) \times 10^{-2}$% in the first case and $(0.3 \pm 0.1) \times 10^{-2}$% in the second. By comparing these values with the measured quantum yield of MV^{+} $(4.0 \pm 1.0) \times 10^{-2}$% on the initial portion of the kinetic curve for its formation, and under similar conditions, we conclude that the efficiency of the "dark" catalytic processes developed for these systems is already relatively high. The reason for the lower quantum yield of hydrogen (as compared with the yield of MV^{+}) is still not clear, though we should see that because of the stoichiometry of reaction (3) the quantum yield of hydrogen cannot be greater than one-half the quantum yield of MV^{+}: one possible cause is the screening effect on the photo-catalyst by the added hydrogen evolution catalysts.

Although the oxidation potential of the oxidised forms of these donors is insufficient to evolve oxygen from water, we note that the oxidation potential E_0 of one of the intermediates ($Zn\text{-}TPP^{+}$, $E_0 = +1.0$ V with respect to the NHE [105]) is high enough if a pH $\geq$ 5 is maintained inside the vesicle. This justifies the hope that the full water decomposition cycle may be realised in the near future in a system based on Zn-TPP and related metallo-porphyrins by optimising the choice of electron donors.

Knowing the mechanism of electron photo-transfer through a bi-layer membrane containing Zn-TPP should assist the solution of important problems such as maximising the quantum yield of the electron photo-transfer and improving the spectral sensitivity of the process, since (at $\lambda > 450$ nm, for example) the useful spectral range is limited by the relatively narrow absorption bands of Zn-TPP (total width 50–100 nm).

Thus, if scheme (II) is correct the rate of electron photo-transfer through the membrane should increase with the rate of regeneration of Zn-TPP molecules from the cation radical $Zn\text{-}TPP^{+}$ formed by the photo-transfer, and with the rate of excitation of Zn-TPP molecules on the inner surface of the membrane by energy transfer through some "antenna", analogous to the chlorophyll molecules in the chloroplasts of plants. We achieved this by using the complex $Ry(bipy)_3^{2+}$ at a concentration of ~0.07 M in the inner cavity of the lecithin vesicles[108] as a sensitising additive, able in principle to bring about both the transfer of an electron from the inner cavity to the $Zn\text{-}TPP^{+}$ and the transfer of energy to Zn-TPP. At this concentration of $Ru(bipy)_3^{2+}$ the absorption spectrum of the vesicle solution contains (in addition to strong Zn-TPP absorption bands) a fairly strong absorption band at $\lambda \cong 460$ nm due to the added sensitiser.

Irradiation of this combined system (containing both Zn-TPP and $Ru(bipy)_3^{2+}$) with light of $\lambda > 415$ nm, which excites both these photosensitive complexes, results in much faster electron photo-transfer through the membrane. Under these conditions we observed the highest ever quantum yield (~0.6%) for the photo-transfer through a membrane to MV^{2+} of an electron in vesicles containing a photocatalyst inside a lipid bi-layer. The quantum yield was calculated as the ratio of the initial rate of electron photo-transfer to the total number of quanta absorbed by the system (i.e. allowing for the absorption of both $Ru(bipy)_3^{2+}$ and Zn-TPP).

The details of the mechanism by which $Ru(bipy)_3^{2+}$ sensitises this system are being studied at the moment. We shall only note that if this sensitising effect is associated with the formation of the strong oxidiser $Ru(bipy)_3^{3+}$ (for which $E_0 = +1.3$ V relative to the NHE) in the inner cavity of the vesicle, for example by a reaction such as

$$Zn\text{-}TPP^{+} + {}^{*}Ru(bipy)_3^{2+} \rightarrow Zn\text{-}TPP + Ru(bipy)_3^{3+}$$

it should be possible (by an appropriate choice of homogeneous catalyst, e.g. a cobalt or iron complex, see Section III) to evolve oxygen from water in the cavity of the vesicle and thus complete the cycle of the photocatalytic decomposition of water.

Indeed, we have found[108] that the processes in this system are affected by the presence of cobalt chloride (an active oxygen evolution homogeneous catalyst) in the inner cavity of vesicles sensitised by the ruthenium complex. Thus, if the Na_2-EDTA solution in the cavity is replaced by a (1–5) $\times$ 10^{-4} M solution of $CoCl_2$ in a borate buffer (pH 9) to allow oxygen evolution a small quantity of MV^{+} is formed during irradiation of the system: if other conditions are kept constant the initial rate of accumulation is always greater in the presence of $CoCl_2$ than in its absence (when, as stated above, the accumulation of MV^{+} is due to the irreversible oxidation of impurities in egg lecithin).

We may suggest that in the presence of $CoCl_2$ the strong oxidiser $Ru(bipy)_3^{3+}$ produced by the irradiation contributes to the catalytic oxidation of water, which under these conditions may be faster than the oxidation of the impurities. However, a final judgement on the possibility of oxidation of water in the inner cavities of vesicles sensitised by $Ru(bipy)_3^{2+}$ must await direct experimental evidence on the presence (or absence) of evolved oxygen.

We note that after the addition of $Ru(bipy)_3^{2+}$ to the vesicle cavity the scheme proposed for this system becomes even more similar to the "Z-scheme" of natural photosynthesis: on the outer surface of the membrane we find the analogue of "photo-system I", and on the inner surface the analogue of "photo-system II".

Some of our latest results[109] show that $Ru(bipy)_3^{2+}$ within the inner cavity of vesicles can act as a photocatalyst and induce electron transfer even if the membrane is "photo-passive" (i.e. if the lipid bi-layer does not contain a photo-catalyst). This photo-transfer takes place in the prescence of photo-inactive compounds (electron carriers) able to penetrate into the lipid bi-layer or to pass through it carrying an electron from the electronically excited state of $Ru(bipy)_3^{2+}$.

Thus when $Ru(bipy)_3^{2+}$ ions in the cavity of lecithin vesicles are excited by light together with the irreversible electron donor $EDTA^{2-}$, and if the lipid membrane contains the water-insoluble electron carriers cetylviologen dibromide

(*N*,*N'*-dicetyl-4,4'-dipyridine, CV^{2+}) or decylviologen (*N*,*N'*-didecyl-4,4'-dipyridine) we observe photocatalytic transfer of an electron from $EDTA^{2-}$ in the inner cavity to the reversible electron acceptor $Fe(CN)_6^{3-}$ in the outer volume of the vesicle, which cannot pass through the lipid membrane. The quantum yield of the electron photo-transfer to $Fe(CN)_6^{3-}$ is strongly dependent on the concentration of the electron carrier in the membrane, reaching (2.3 ± 0.5)% in the case of CV^{2+} for a molar ratio of CV^{2+} : lipid = 1 : 100, and (15 ± 5)% for a molar ratio of CV^{2+} : lipid = 1 : 20 (temperature 293 K, excitation of the $Ru(bipy)_3^{2+}$ by monochromatic light of wavelength 488 nm at a radiation density of 1.0 W cm^{-2}. local concentrations of $Ru(bipy)_3^{2+}$, $EDTA^{2-}$, and $Fe(CN)_6^{3-}$ 1.6×10^{-3}, 0.2, and 10^{-3} M respectively).

Photocatalytic electron transfer through these membranes was observed also after replacing the $Fe(CN)_6^{3-}$ outside the vesicle by two-electron acceptors such as the water-soluble dyes of the phenothiazine series (Methylene Blue, thionine); the quantum yield of the electron transfer through the lipid bi-layer under these conditions was again of the order of several per cent.

We should stress that the quantum yields for electron transfer quoted above are much higher than the usual values for the "photo-active" membrances (containing a photo-catalyst within the membrane) discussed in this review. Therefore the long-term prospects of photocatalytic systems based on photo-passive membranes are also good.

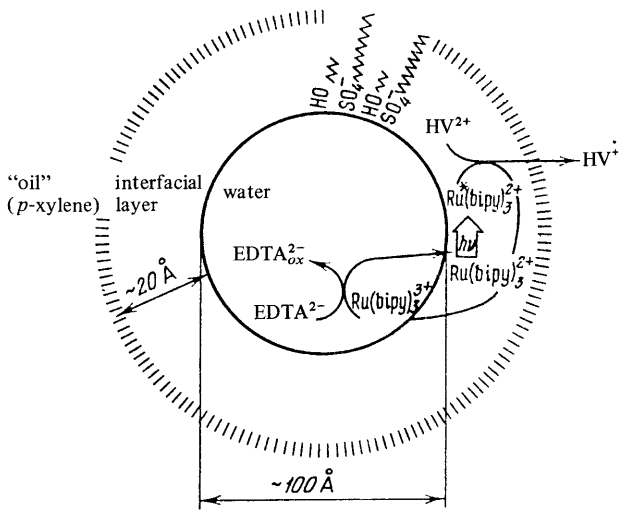


Figure 16. Scheme of the photo-transfer of an electron between phases in an anionic ME-I micro-emulsion of the "water in oil" type containing heptylviologen (*N*,*N'*-diheptyl-4,4'-dipyridine) HV^{2+}, $Ru(bipy)_3^{2+}$, and $EDTA^{2-}$.

2. Charge Separation in Micro-emulsions

The recombination of the products of reaction (1) can be suppressed also by using micro-emulsions of the "water in oil" type. We have studied the following micro-emulsion compositions (in wt.%): *p*-xylene (60.8%), n-pentanol (22.0%), sodium dodecyl sulphate (3.6%), and water (13.6%) (micro-emulsion ME-I [110,111]), and also toluene (71.3%), n-pentanol (7.4%), decylammonium propionate (9.1%), and water (12.2%) (micro-emulsion ME-II [111]). Both are transparent, slightly opalescent solutions containing water drops ~100 Å in diameter in *p*-xylene [112] or toluene. These droplets are surrounded by a layer on n-pentanol molecules and partially dissociated molecules of sodium dodecyl sulphate (SDS) in the emulsion ME-I, or of decylammonium propionate (DAP) in ME-II, which create an interface ~20 Å thick. The structure of ME-I is shown in Fig. 16.

The photocatalysts added to the micro-emulsion were the complex $Ru(bipy)_3^{2+}$ or its surface-active analogue $Ru(C_{17}\text{-bipy})(bipy)_2^{2+}$, which differs from $Ru(bipy)_3^{2+}$ in having one bipyridyl ligand replaced by a bipyridyl derivative (4-methyl-4'-heptadecyl-2,2'-bipyridyl) with a long hydrophobic cetyl chain in the fourth position[113]. By comparing data on the rate of fluorescence quenching of the ruthenium(II) complexes in homogeneous aqueous solutions and in micro-emulsions by substances readily soluble in water but poorly soluble in *p*-xylene or toluene (see Table 4) we conclude that the ruthenium photocatalysts are found mainly at the interface. Thus the large decrease in the quenching rate constant produced by changing from homogeneous solutions to micro-emulsions shows that the photocatalysts are not localised in the aqueous phase. On the other hand they cannot be localised in the organic phase, because if they were they could not interact with the quenchers (which are in the water phase) with the observed rate constants of $k_q \geq 10^7$ litre $mole^{-1}$ s^{-1}.

Table 4. Rate constants k_q for the luminescence quenching of ruthenium(II) complexes in homogeneous solutions and in micro-emulsions at 297 K .

Complex	A	10^3[A], M	10^{-8} k_q, litre $mole^{-1}$ s^{-1}
	medium: water		
$Ru(bipy)_3^{2+}$	MV^{2+}	5	4.7
$Ru(bipy)_3^{2+}$	HV^{2+}	5	8.0
	medium: ethanol + toluene (1 : 1)		
$Ru(bipy)_3^{2+}$	CV^{2+}	1	6.1
	medium: ME-I		
$Ru(bipy)_3^{2+}$	MV^{2+}	4—25	0.8
$Ru(bipy)_3^{2+}$	HV^{2+}	4—25	0.5
$Ru(bipy)_3^{2+}$	CV^{2+}	3	2.5
$Ru(C_{17}\text{-bipy})(bipy)_2^{2+}$	MV^{2+}	4—25	0.5
$Ru(C_{17}\text{-bipy})(bipy)_2^{2+}$	HV^{2+}	4—25	0.9
$Ru(C_{17}\text{-bipy})(bipy)_2^{2+}$	CV^{2+}	3	4.6
	medium: ME-II		
$Ru(bipy)_3^{2+}$	CV^{2+}	1	8.0
$Ru(C_{17}\text{-bipy})(bipy)_2^{2+}$	CV^{2+}	1	8.8

Notes. A is the quencher. For the micro-emulsions the local concentrations of the water-soluble MV^{2+} and HV^{2+} are given on the assumption that these species are present only in the water phase. In the case of the water-insoluble CV^{2+} the concentration is calculated in terms of the whole volume. The effective bimolecular quenching rate constants were obtained by dividing the quenching rate by the concentrations as defined above.

Irradiation with visible light ($\lambda > 450$ nm) of the micro-emulsion ME-I containing, in addition to the photocatalyst [$Ru(bipy)_3^{2+}$, 6×10^{-5} M], an electron acceptor (heptylviologen, HV^{2+}, 3×10^{-4} M) and an electron donor (Na_2-EDTA, 6×10^{-3} M) localised mainly in the water phase, causes accumulation of the cation radicals HV^{+} with a quantum yield of

~1%.[110] In the absence of Na_2-EDTA or of the ruthenium complex no $HV^{+\cdot}$ is formed. Photolysis of a homogeneous aqueous solution containing $Ru(bipy)_3^{2+}$, HV^{2+}, and Na_2-EDTA produces a violet precipitate of water-insoluble $HV^{+\cdot}$ which can be extracted easily and quantitatively by a mixture of *p*-xylene and n-pentanol in the same ratio as in the micro-emulsion. This shows that the $HV^{+\cdot}$ cation radical formed by photolysis of the ME-I micro-emulsion must also reside mainly in the organic phase. The electron donors ($EDTA^{2-}$ anions) cannot be accommodated in the interface (saturated with SDS anions) or in the non-polar organic phase, and therefore they can only be in the aqueous phase of the micro-emulsion. Since we are able to achieve almost complete reduction of HV^{2+} to $HV^{+\cdot}$ it appears that the $Ru(bipy)_3^{2+}$ present at the interface in an amount five times smaller than the heptylviologen acts as a true photocatalyst for the transfer of an electron from the donor $EDTA^{2-}$ (localised in the water phase) to the acceptor HV^{2+} (whose reduced form is extracted into the organic phase).

Flash photolysis of a homogeneous aqueous solution containing only $Ru(bipy)_3^{2+}$ and HV^{2+} produces the cation radical $HV^{+\cdot}$, whose concentration then decreases as a result of recombination with the oxidiser $Ru(bipy)_3^{3+}$ formed together with the $HV^{+\cdot}$. The disappearance of $HV^{+\cdot}$ obeys the law of second-order kinetics with a rate constant $k = (1.5 \pm 0.1) \times 10^9$ litre^{-1} s^{-1} up to an extent of reaction of 99%. In contrast, the decrease in optical density of $HV^{+\cdot}$ after flash photolysis of an ME-I micro-emulsion containing only $Ru(bipy)_3^{2+}$ and HV^{2+} is kinetically more complex (see curve *1* of Fig.17). At short times we observe a bimolecular disappearance of $HV^{+\cdot}$ with a rate constant $k = (1.2 \pm 0.1) \times 10^9$ litre mole^{-1} s^{-1}, but after ~1 ms the disappearance of $HV^{+\cdot}$ slows down and the bimolecular law is not obeyed.

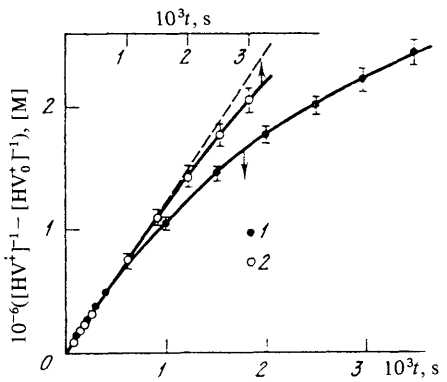


Figure 17. Kinetic curves for the recombination of $HV^{+\cdot}$ with $Ru(bipy)_3^{3+}$ (*1*) and of $HV^{+\cdot}$ with $Ru(C_{17}\text{-bipy})(bipy)_2^{3+}$ (*2*) after flash photolysis of an ME-I micro-emulsion containing 3.1×10^{-3} M HV^{2+} and 2.5×10^{-4} M ruthenium complexes; temperature 298 K. The broken line denotes second-order kinetics with the rate constants calculated from the initial portions of the experimental kinetic curves[110].

This type of recombination kinetics can be explained as follows (a more detailed analysis can be found in Ref.110). During the photolytic flash one of the primary products of electron photo-transfer at the interface (the species $HV^{+\cdot}$) can distribute itself between the interface and the organic phase in accordance with its solubility, whereas the second product [$Ru(bipy)_3^{3+}$] diffuses slowly into the aqueous phase where it can oxidise $EDTA^{2-}$ if this species is present. The initial portion of the kinetic curve, described by the bimolecular law, corresponds to recombination of the $HV^{+\cdot}$ with the $Ru(bipy)_3^{3+}$ which has not yet migrated into the water phase. The slowing down of the recombination observed at long times shows that some of the oxidiser $Ru(bipy)_3^{3+}$ has migrated away from the sphere of action and is no longer available to recombine with the $HV^{+\cdot}$ in the interfacial layer.

This explanation of the shape of curve *1* in Fig.17 suggests that the replacement of $Ru(bipy)_3^{2+}$ by the more lyophilic complex $Ru(C_{17}\text{-bipy})(bipy)_2^{2+}$ should result in less marked deviations of the recombination kinetics from the bimolecular law, since the transfer of the oxidised form of the photocatalyst from the interface to the aqueous phase would then be hindered. As curve *2* of Fig.17 shows, this prediction is borne out in practice.

Table 5. Recombination rate constants k and relative probabilities P/P_0 of the oxidiser and the reducer formed by electron photo-transfer from a donor to an acceptor emerging from the original pair in homogeneous aqueous solutions and in micro-emulsions at 298 K.[111]

Donor	Acceptor	$10^8\,k(\pm1)$, $M^{-1}\,s^{-1}$	P/P_0
	medium: water		
$Ru(bipy)_3^{2+}$	MV^{2+}	17	1.00
$Ru(bipy)_3^{2+}$	HV^{2+}	15	0.95
	medium: ME-I		
$Ru(bipy)_3^{2+}$	MV^{2+}	25	0.24
$Ru(bipy)_3^{2+}$	HV^{2+}	12	0.67
$Ru(bipy)_3^{2+}$	CV^{2+}	12	0.15
$Ru(C_{17}\text{-bipy})(bipy)_2^{2+}$	HV^{2+}	7.8	0.35
ditto	CV^{2+}	8.0	0.15
	medium: ME-II		
$Ru(bipy)_3^{2+}$	CV^{2+}	2.7	2.8
$Ru(C_{17}\text{-bipy})(bipy)_2^{2+}$	CV^{2+}	6.7	0.7

Notes. In the case of water solutions the k values are given for a low ionic strength ($\mu < 0.05$ M); P_0 is the probability of the electron photo-transfer products emerging from the original pair in the $Ru(bipy)_3^{2+}$–MV^{2+} system in aqueous solution; the precision of the measurements of P/P_0 is ±10%.

Thus, owing to the fast extraction of $HV^{+\cdot}$ into the organic phase coupled with a much slower migration of $Ru(bipy)_3^{3+}$ into the water phase, some of the primary products of the electron photo-transfer process are in different phases, and as a result their recombination is suppressed. These results justify the hope that effective segregation of the products of primary electron photo-transfer into different phases may be achieved in the near future by varying the electric charge of the interfacial layer of the micro-emulsion and the hydrophilic and oleophilic properties of the primary electron donor and acceptor (by introducing appropriate substituents).

Thus, by varying these properties we should be able to control the two most important parameters of the system, responsible in the final analysis for effectiveness of the extraction of the primary charge separation products: the effective rate constant k for the recombination of the primary oxidiser and reducer in the interfacial layer of the micro-emulsion and the probability P of the oxidiser and the

reducer breaking away from their initially paired configuration. We note that a marked deviation of the parameter P from unity is the most usual explanation of small quantum yields in bimolecular oxidation–reduction reactions involving excited states. Our values[111] of k and P for the micro-emulsions ME-I (with a negatively charged interfacial layer) and ME-II (positively charged layer) are listed in Table 5 for different pairs of electron donor and electron acceptor having different lyophilicities. The rate constant k was measured from the initial slope of the kinetic curve for the recombination of the primary oxidiser and reducer, recorded by the flash photolysis method. The probability P was determined by comparing the initial concentrations of the reduced forms of the viologens, observed immediately after a photolytic light flash of duration less than 10^{-5} s, with the concentration of MV^{+} observed under similar conditions in a homogeneous aqueous solution containing $Ru(bipy)_3^{2+}$: the absolute value of the probability P for the $Ru(bipy)_3^{2+}$–MV^{2+} system in water was found[114] to be 25%.

It is clear from Table 5 that, as expected, the best results (i.e. a more than six-fold decrease in k and an almost three-fold increase in P to $P = 2.8 \times 25\% = 70\%$ as compared with a homogeneous aqueous solution) are obtained in micro-emulsions with a positively charged interface if the electron donor has a low lyophilicity [$Ru(bipy)_3^{2+}$] and the electron acceptor has the highest possible lyophilicity (cetylviologen, CV^{2+}). A positive charge on the interface of the micro-emulsion prevents the charge separation products of the same (i.e. positive) sign from recombining at the phase boundary.

We note that in a really effective photo-catalytic system the recombination of the D^{+} and A^{-} particles created by reaction (1) should be slow enough to allow reactions (2) and (3) to proceed, with evolution of hydrogen and oxygen. We should stress that the reduced forms of HV^{+} and CV^{+} (like the reduced form MV^{+}) can evolve hydrogen from water in the presence of the catalysts discussed in Section II; the prospects of the evolution of oxygen from water by $Ru(bipy)_3^{3+}$ and its analogues are discussed in Section III.

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This general assessment of the present state of photocatalytic converters of solar energy into chemical energy by exploiting the water decomposition reaction shows that the development of effective charge separation systems continues to be the major problem facing the creation of practical molecular photocatalytic systems for decomposing water into hydrogen and oxygen. We may hope that as soon as these systems are discovered the efficient decomposition of water by sunlight under laboratory conditions will be a practical possibility.

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