Some aspects of photochemical systems for direct light-induced hydrogen production

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Abstract

Various possible pathways for photochemical conversion of light energy, including light-induced electron transfer and hydride transfer, are described. Several problems diminishing the photoconversion efficiency as well as side reactions affecting the stability of these systems are discussed. Oxidation of photosensitizers by singlet oxygen as well as attack by OH^- radicals is supposed to be the main degradation pathway for dyes and for other photoinduced reactions. The stability of viologens (acting as electron transfer agents) is mainly affected by hydrogenation, for which a reaction mechanism is presented. The dependence of rate constants on the free enthalpy of reaction is discussed with respect to quantum yields for light energy conversion. Following this, quantum yields of cyclic water splitting based on diffusion-controlled reactions are very low. Selective catalysis or vectorial processes (with a spatial charge separation) could enhance the quantum yields.

1. Introduction

The anthropogeneous changes in the atmosphere caused by the combustion of fossil fuels (oil, coal and gas) and the destruction of large forest areas are responsible for an intensive disturbance of the biosphere. Carbon dioxide can be considered as the most important constituent of the atmosphere that is effectively altered by mankind. Since the beginning of industrialization the concentration of CO_2 has increased from 280 to 350 ppm [1] and a further rise up to 700 ppm by the year 2050 has been predicted [1-5]. It is commonly agreed that CO_2 makes (besides CH_4, NO_x, and FCH) a major contribution to the greenhouse effect. This has led to a growing interest in new non-fossil energy supplies, especially solar energy. Since solar energy is neither permanent nor constant in intensity the world over, an energy carrier is needed which can perform the functions of storage and transportation of energy. Such an energy carrier could be hydrogen [3-5]. The use of solar energy in combination with hydrogen is considered an ideal system for supplying energy in the future [3-5].

A large number of research groups have studied the production of H_2 by solar heat, by electrolysis (combined with photovoltaics) and by direct conversion of solar energy with photochemical or photobiological systems [6-15]. Besides the usage of photovoltaics and electrolysis for the solar generation of hydrogen, photochemical systems for direct light-induced hydrogen production and water splitting have also been investigated intensively [16-28].

In the field of direct water splitting one can make a rough classification of systems into homogeneous and heterogeneous systems, in which the main step of light-induced charge separation proceeds either by a homogeneous (diffusion-controlled) reaction (in solution) or (in the heterogeneous case) in a semiconductor. In the latter case a (built-in) electric field is mainly responsible for the charge separation. As a simple concept we wish to propose that the electric field (of a p–n or Schottky junction) could be used as a main feature to distinguish between homogeneous and heterogeneous systems. Systems involving semiconductor powders or photoelectrodes (e.g. TiO_2, WO_3, ZnO, SiC, CdS, CdSe, GaP, GaAsP, GaAs, Si) have been investigated widely [29-31]. Two main problems are still being debated: stability of the semiconductor (corrosion) and absorbance suitable for solar applications (e.g. TiO_2 is a very stable semiconductor but has a band gap of 3.2 eV [31], allowing only a small part of the solar light to be absorbed). However, in this paper the focus will mainly be on homogeneous systems.

For experimental details of the work reported in this paper see Refs. [32-40].

2. Homogeneous systems involving light-induced electron and hydride transfer

In the field of homogeneous photochemical water splitting and H_2 formation, various systems involving light-induced electron transfer reactions and proton transfer or hydride transfer as the basic reaction for light conversion have been studied [16–28,32–46].

2.1. Systems based on light-induced hydride transfer

In organic photochemistry, benzophenone is a widely used photosensitizer which in its excited state and in the presence of a platinum catalyst is capable of oxidizing secondary alcohols to give ketones and hydrogen [41,44–47]. For the reaction mechanism see Scheme 1.
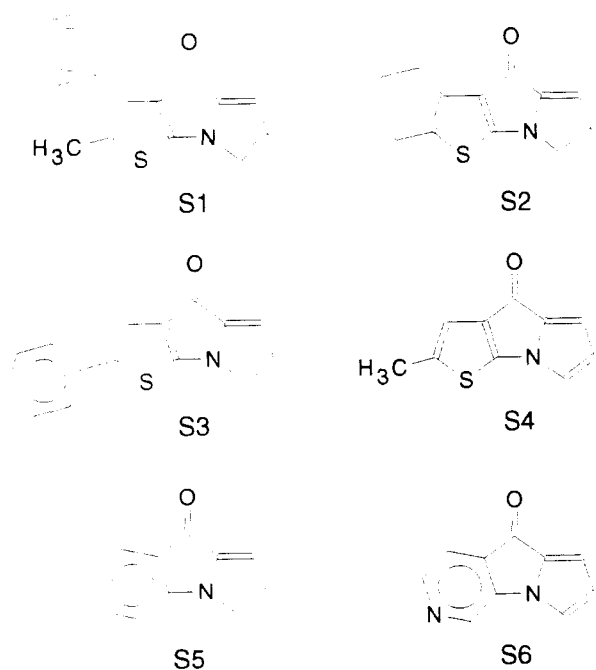

Scheme 1.

Scheme 2.
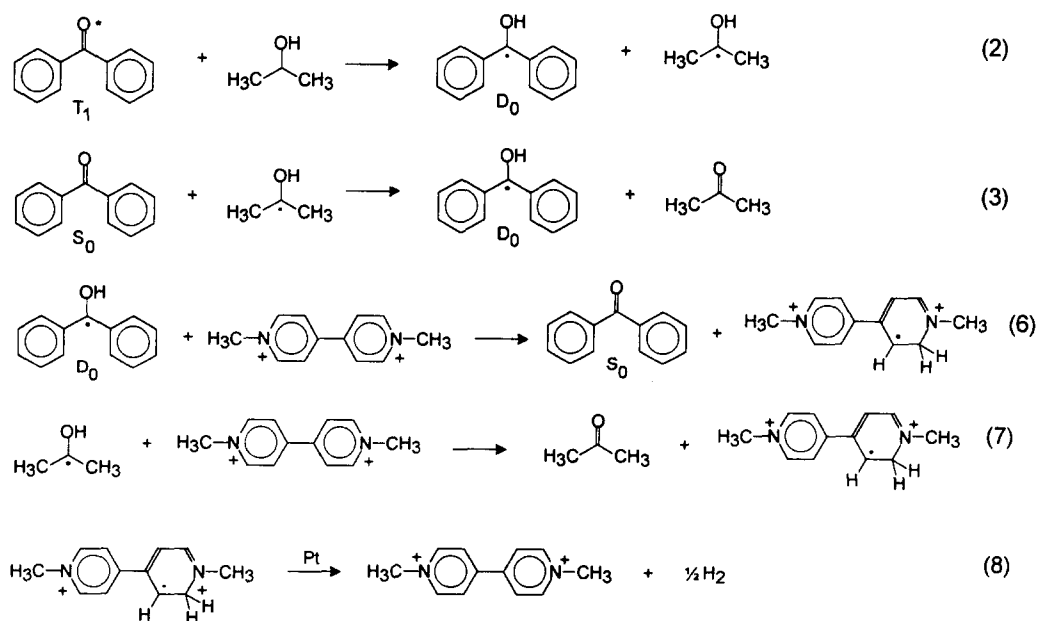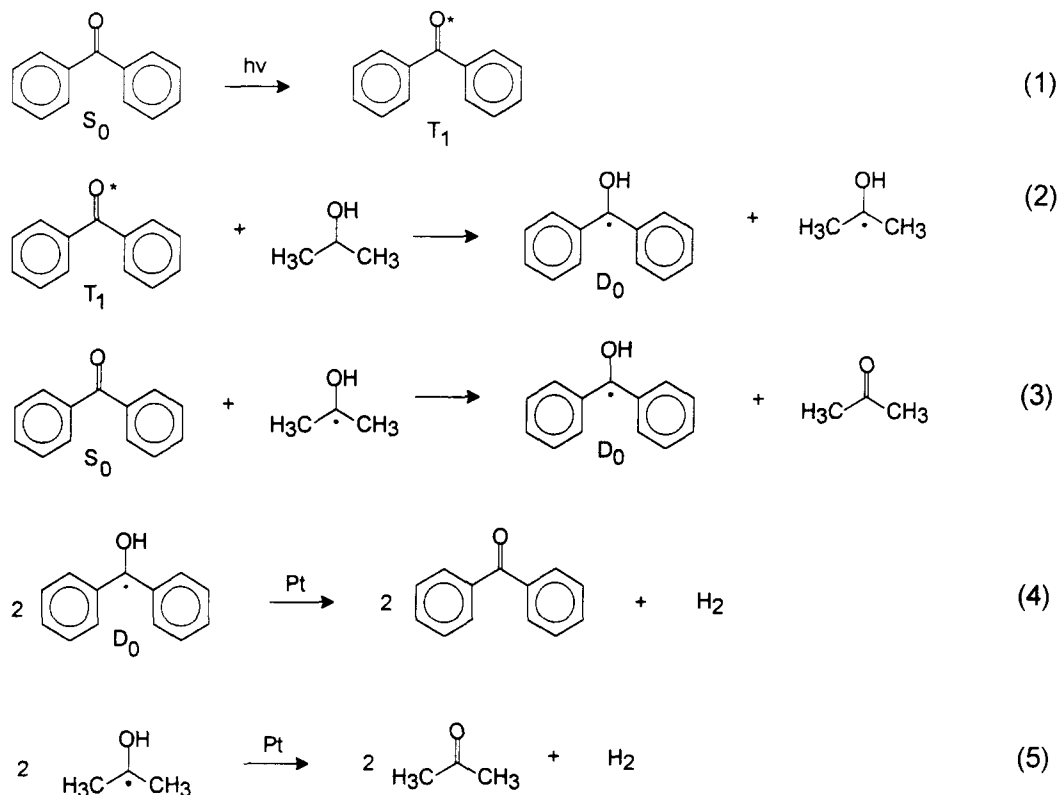
Fig. 1. Polycyclic aromatic ketones (thieno[2,3-b]pyrrolizinone derivatives S1–S6). Structures like these were tested for light-induced hydrogen evolution via a hydride transfer mechanism (with low success).

The addition of methyl viologen (MV^{2+}; 1,1'-dimethyl-4,4'-bipyridinium dication), acting as an electron relay compound, increases the quantum yield of light-induced hydrogen formation (see Scheme 2).

However, one great disadvantage of these systems is that benzophenone does not absorb in the visible light region and therefore its practical application for conversion of solar energy is limited. Several other dyes of the benzophenone type (fluorenone and its derivatives, pyrrolizinone, etc.) have been investigated with respect to a bathochromic shift of the absorption (maximum) and to light-induced H_2 formation [38,39]. It was shown that suitable modifications of the structure of polycyclic aromatic ketones (e.g. thieno[2,3-b]-pyrrolizinone derivatives; see compounds S1–S6 in Fig. 1) give stronger absorbances and a bathochromic shift of the lowest energy absorption band. However, although compounds S1–S6 possess higher absorption coefficients in the visible light region, (efficient) visible light-induced hydrogen formation could not be achieved. The low quantum yields were attributed to the following reasons. The lowest excited singlet state S_1 (n–π^*) of compounds S1–S6, responsible for the visible absorption, was not able to oxidize secondary alcohols, e.g. 2-propanol. Hence visible-light-induced hydrogen formation could not be observed with compounds S1–S6. Using the second excited singlet state S_2, a high excitation energy ($\lambda < 300$ nm) is necessary. Irradiation with wavelengths $\lambda < 300$ nm led to a small amount of hydrogen with quantum yields $\phi_{\frac{1}{2}H_2} < 0.001$. The small quantum efficiencies achieved were explained by steric effects. The hydride transfer reaction from the secondary alcohol to affect the excited state of the keto compound requires a suitable configuration

of the transition state, including the formation of sp^3 orbitals of the carbonyl carbon atom accompanied by changes in bonding angles (and lengths). Owing to the rigid structure of compounds S1–S6, these changes are very hindered, causing the observed small reaction rates. On the other hand, these rigid structures are also responsible (from this same viewpoint) for the bathochromic shift of the low energy absorption.

Although the benzophenone system (and its analogues, e.g. the thieno[2,3-b]pyrrolizinone derivatives S1–S6) is an interesting model system to study the photochemical reactions (with UV light) that are, for example, not affected by pH [43], its practical application for solar energy conversion is not feasible.

2.2. Systems based on light-induced electron transfer

2.2.1. Principle of light-induced water splitting

The second system which has been investigated extensively during the past 20 years [17–27,33,34,48–51] is based on light-induced electron transfer reactions and seems to be more promising.

After excitation of a photosensitizer S, charge separation takes place:

$$S + h\nu \longrightarrow S^* \tag{9}$$

$$S^* + D \longrightarrow S^- + D^+ \tag{10}$$

$$S^* + R \longrightarrow S^+ + R^- \tag{11}$$

Since the photosensitizer is in its excited state, it is both a stronger oxidant and reductant than in its ground state because of its higher energy content. The light-induced charge separation can result either in a reduced S^- (systems employing oxidative quenching (Eq. (10))) or in an oxidized photosensitizer S^+ (reductive quenching (Eq. (11); see also Fig. 2) [52,53]. Whether oxidative quenching (10) or reductive quenching (11) takes place depends on the redox potentials
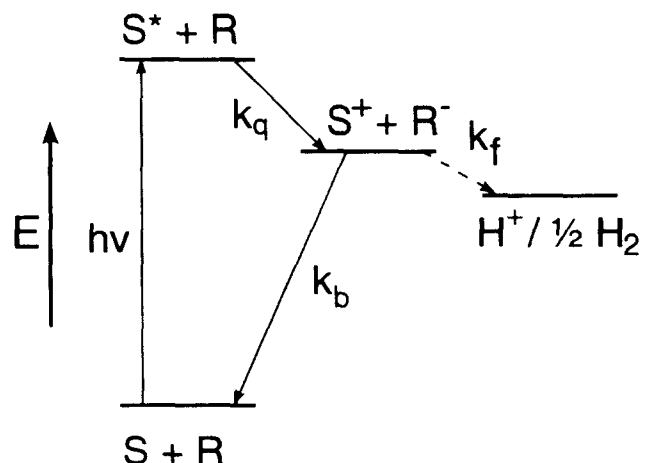

Fig. 2. Energy diagram for light-induced charge separation: S, photosensitizer; R, electron relay (electron acceptor); k_q, rate constant for quenching reaction; k_b, rate constant for back electron transfer reaction; k_f, rate constant for forward reaction (proton reduction).
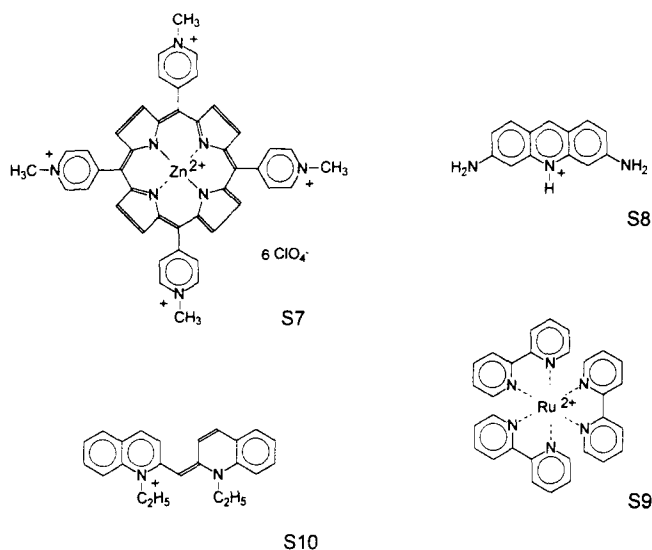
Fig. 3. Widely used photosensitizers: S7, zinc porphyrin; S8, proflavine; S9, Ru(bpy)$_3^{2+}$; S10, 1,1'-dimethyl-2,2'-cyanine dye.
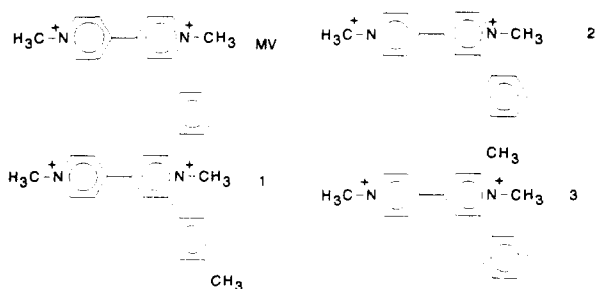

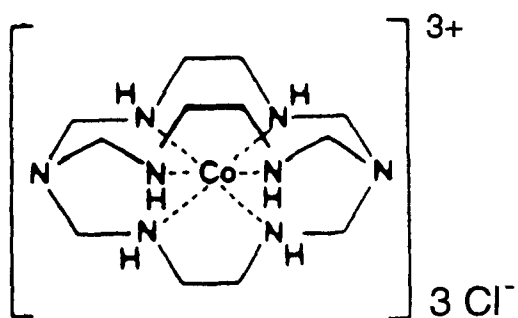Fig. 4. Methyl viologen (MV^{2+}; 1,1'-dimethyl-4,4'-bipyridinium dication) and derivatives R1–R3.

Fig. 5. Cobalt sepulchrate (Co(sep)$^{3+}$; 1,3,6,8,10,13,16,19-octazazbicyclo[6.6.6]eicosane cobalt trichloride).

of the species involved. When the "molecular electronegativity" Δ_{ME} of a compound M is defined as the sum of the reduction and oxidation potentials, i.e. $\Delta_{ME} = E^\circ(M/M^+) + E^\circ(M^-/M)$, then that compound acts as an electron acceptor which possesses a larger Δ_{ME} [52].

In both cases the light-induced electron transfer reaction results in a pair of products ($S^+ + R^-$ or $S^- + D^+$) which possess a higher energy content and can undergo further reactions (see Fig. 2). Light-induced intermolecular electron transfer reactions are usually fast (e.g. for Ru(bpy)$_3^{2+*}$ (S) quenched by viologens (R), $k_q \approx 10^9$ l mol^{-1} s^{-1} [32]) and
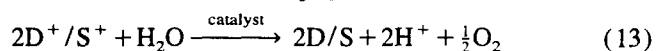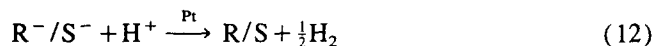
thus (in solutions) only limited by diffusion processes [16,54]. Fast electron transfer (quenching) reactions are necessary, since the photosensitizer's excited state lifetime is usually short (e.g. for ^{3}Ru(bpy)$_3^{2+*}$, $\tau_0 = 0.64$ μs [52]).

By thermal back reaction (k_b in Fig. 2) the initial state S + R is reached, producing heat. During the lifetime of the charge-separated state $S^+ + R^-$ (usually less than 1 μs), other reactions (e.g. proton reduction and hydrogen formation; k_f in Fig. 2) can occur.

Ruthenium polypyridine complexes (e.g. Ru(bpy)$_3$Cl$_2$) [48,49,54–62] as well as porphyrins [63–69] and organic dyes such as proflavine [61,62] or cyanine dyes [70–77] have been investigated as photosensitizers (S7–S10; see Fig. 3). Depending on the photosensitizer, various types of electron acceptors and donors have been studied, including viologens (1,1'-dialkyl-4,4'-bipyridinium dications; see Fig. 4 [24,25,34,78–88]), polypyridinium metal complexes [48,55,89], Wilkinson catalysts [90–92] and cobalt cage complexes (e.g. cobalt sepulchrate [55,93–99]; see Fig. 5).

After successful light-induced charge separation, other consecutive processes have to be introduced in order to get some storable products and to avoid the (thermal) back reaction (k_b). Such consecutive processes could be, for example, hydrogen and oxygen formation (or CO$_2$ reduction).

In the case of cyclic water splitting (see Fig. 6(a)) the reduced electron acceptor R$^-$ (or photosensitizer S$^-$ in the case of oxidative quenching according to Eq. (10)) should reduce protons to hydrogen (in the presence of a suitable catalyst, e.g. Pt [78,100–102], RuO$_2$ [103,104], Pd [32] or Ni [105,106]) and the oxidized sensitizer S$^+$ (or electron donor D$^+$) should oxidize water to oxygen:

$$R^-/S^- + H^+ \xrightarrow{\text{Pt}} R/S + \tfrac{1}{2}H_2 \tag{12}$$

$$2D^+/S^+ + H_2O \xrightarrow{\text{catalyst}} 2D/S + 2H^+ + \tfrac{1}{2}O_2 \tag{13}$$

This also requires a suitable catalyst (e.g. RuO$_2$ or IrO$_2$ [107–110]) and still has to overcome additional drawbacks, e.g. RuO$_2$ is subject to corrosion (oxidation to the inactive RuO$_4$ [111]). Moreover, cyclic water splitting requires catalysts which are selective for the forward reaction (i.e. H$_2$ and O$_2$ formation) and which do not increase the rate constants of back reactions [112].

The overall reaction would be cyclic light-induced water splitting with oxygen and hydrogen as desired products.

In order to study the hydrogen evolution, a "sacrificial" electron donor was introduced several years ago [28,48,113,114], mimicking the oxygen evolution process and reducing the oxidized sensitizer (see Fig. 6(b)) and thus diminishing the back electron transfer. EDTA (ethylenediaminetetraacetic acid) and TEA (triethanolamine) were the mostly used "sacrificial" electron donor substances. With such "sacrificial systems", quantum yields ($\phi_{\frac{1}{2}H_2}$) up to 18% can be achieved [34]. The components S and R are not consumed during this cyclic reaction but may be destroyed as a result of different competing and consecutive processes.
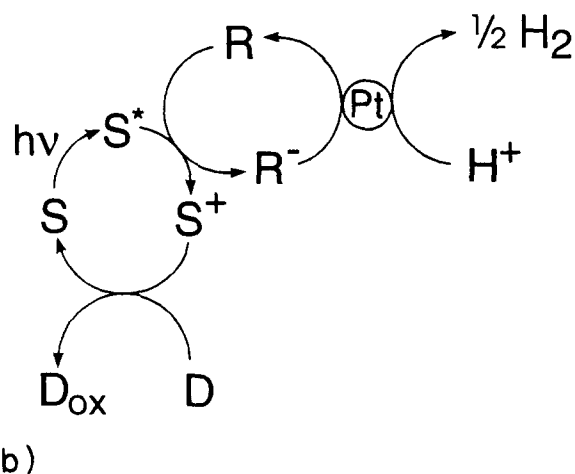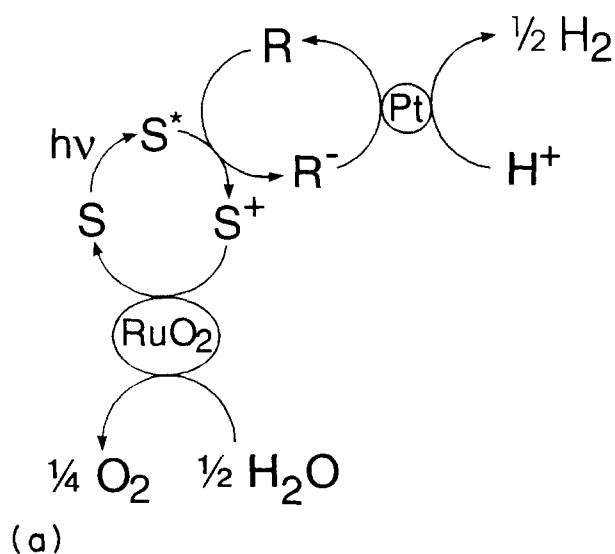
Fig. 6. Reaction schemes for (a) light-driven cyclic water splitting and (b) light-induced "sacrificial" hydrogen formation: S, photosensitizer (e.g. S7–S9); R, electron relay (electron acceptor; e.g. MV^{2+}, R1–R3); D, "sacrificial" electron donor (e.g. EDTA, TEA); Pt, colloidal platinum catalyst; RuO_2, colloidal ruthenium oxide catalyst.
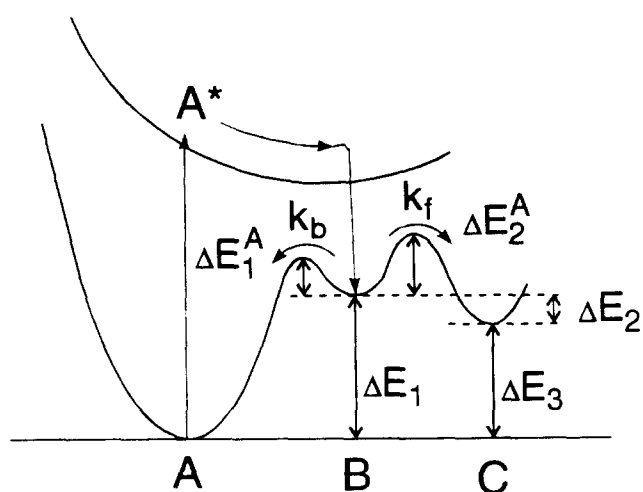

Fig. 7. Energy scheme for light-induced hydrogen formation: $A = S + R + H^+$; $A^* = S^* + R + H^+$; $B = S^+ + R^- + H^+$; $C = S^+ + R + \frac{1}{2}H_2$; see also description in text.

2.2.2. Quantum efficiency and stability

Based on the above-reported model, the quantum yield of a light-induced cyclic water-splitting process depends on the following efficiencies of the single reactions:

(1) the luminescence quantum yield and the efficiency of generation of the charge-separated state $S^+ + R^-$, the latter depending on the rate constants of the quenching reaction (k_q) and of the forward (k_f) and back (k_b) electron transfer reactions:

(2) the reaction rates of H_2 and O_2 formation, which competes with various side reactions.

Therefore a high luminescence quantum yield (in the absence of the quencher), a fast quenching reaction (forward electron transfer) and a slow back reaction are required. The dependence of the rate constant on the standard free enthalpy of reaction is one of the main problems of cyclic water splitting.

2.2.2.1. Relation between rate constants and free enthalpy of reaction

As mentioned above, the quantum yield for the photochemical storage of light energy depends strongly on the forward and back reaction rates. Following the theories of Marcus, Weller and others [115–120], the rate constant of electron transfer reactions, k, can be expressed as a function of the (standard) free enthalpy of reaction, ΔG°:

$$k = \kappa A \sigma^2 \exp\left(\frac{-\Delta G^*}{RT}\right)$$

According to Marcus and Sutin [116],

$$\Delta G^* = w^r + \frac{\lambda}{4}\left(1 + \frac{\Delta G^{\circ\prime}}{\lambda}\right)^2$$

with

$$\Delta G^{\circ\prime} = \Delta G^\circ + w^p - w^r$$

where $A\sigma^2$ has dimensions of collision frequency, σ is the average centre-to-centre distance in the reacting pair during electron transfer and ΔG^* is the free energy of activation, which is related to λ (reorganization energy), ΔG° (standard free energy of reaction in the prevailing medium) and w^r and w^p (work bringing the reactants and products respectively to the mean separation distance σ). Alternatively, according to Rhem and Weller [117],

$$\Delta G^* = \Delta G^\circ + \frac{\Delta G^*(0)}{\ln 2}\ln\left[1 + \exp\left(-\frac{\Delta G^\circ \ln 2}{\Delta G^*(0)}\right)\right]$$

As a brief conclusion (of all theories), it can be said that with more negative standard free enthalpies of reaction, ΔG°, a faster electron transfer reaction is observed (with the exception of the Marcus inverted region).

Considering the simple model of an energy scheme for light-induced H_2 formation (see Fig. 7) and applying the Marcus theory (non-inverted region), a faster back reaction and a slower (forward) hydrogen formation are observed

owing to the differences in the $\Delta G°$ values. In Fig. 7, A stands for the starting position (photosensitizer S in its ground state, relay compound R and protons), A* is the "excited state" of the system (i.e. excited photosensitizer S*, relay compound in its initial state R and protons H$^+$) and B describes the intermediate charge-separated state $(S^+ + R^- + H^+)$ which can either react forward to the products with the energetic level C $(S^+ + R + \frac{1}{2}H_2)$ or react back to the starting point A. In a first-order approximation one can neglect entropy effects and assume $\Delta E \approx \Delta G°$. Since the $\Delta G°$ value for the formation of H_2 (B→C) must be smaller than that for the back reaction (B→A) (otherwise no light energy could be stored) and following Marcus theory (in the non-inverted region), the back reaction is faster than the forward reaction. Thus the quantum yields will be very small if no "sacrificial" electron donor in (large) excess is used. However, this evaluation of electron transfer in terms of thermodynamic driving force does not include geometric factors such as the relative orientation of and distance between the reacting pair. Nevertheless, this should not change the principal result of this short evaluation of electron transfer kinetics. (Further work on this topic is under way [121].)

In principle, various possibilities exist for increasing the quantum yield of cyclic light-induced water splitting [122–132]:

(1) multiphoton processes where more than one photon is used for cyclic water splitting $(\frac{1}{2}H_2 + \frac{1}{4}O_2)$;

(2) vectorial processes yielding a spatial charge separation;

(3) selective catalysts (especially for oxygen evolution);

(4) excess of "sacrificial" electron donor.

Much effort has been made in the case of spatial charge separation by using a micellar environment and modified relay substances or vesicles. Upon substituting one of the methyl groups in MV^{2+} by a long aliphatic chain (e.g. $-(CH_2)_{14}CH_3$), a viologen compound (V^{2+}) is obtained which possesses a novel feature: in its oxidized state (V^{2+}) it exhibits hydrophilic properties, while in its reduced state $(V^{•+})$ it shows hydrophobic behaviour. Using a micellar system, the reduced viologen $V^{•+}$ could be protected by a micelle from the back reaction (with the hydrophilic photosensitizer S^+). If a colloidal catalyst were present in the micelle, reduction of protons could occur. Applying this system, back reactions were found to be about 100 times slower compared with systems without micelles [124–126,133].

Another very promising possibility would be the use of organized systems as in natural photosynthesis. In biosystems the molecules are organized in complex functional entities with cooperating components of molecular dimensions. Well-organized assemblies with suitable configurations of involved reaction centres as in nature have been proposed for the successful conversion of light energy [40,127–132]. Besides porphyrin–quinone-based model compounds mimicking primary processes of photosynthesis [131,134–136], J-aggregate-forming cyanine dyes (see e.g. Fig. 8) and other supermolecular assemblies have also been used for studying
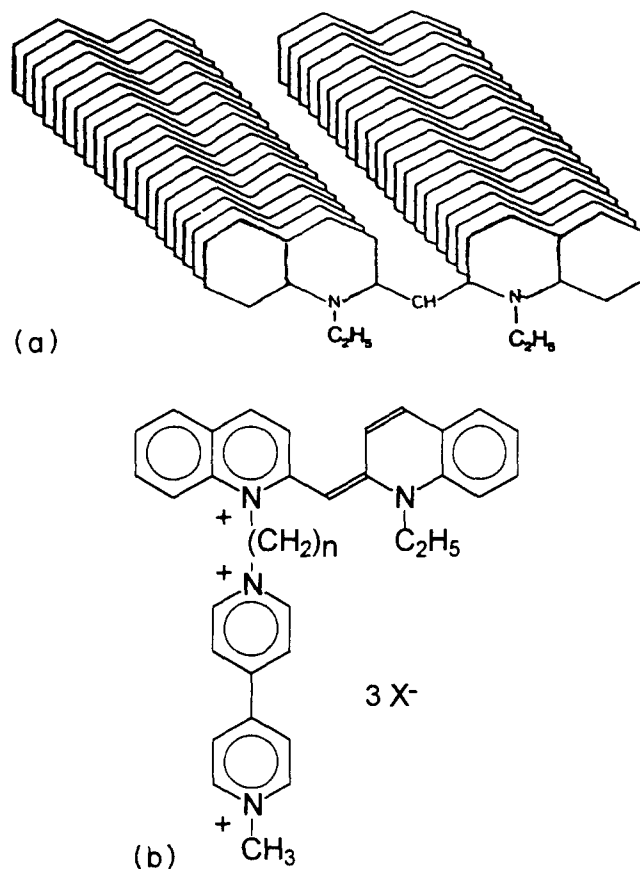

Fig. 8. (a) Simple model of a J-aggregate of a cyanine dye (e.g. S10). (After Refs. [71,72].) (b) Cyanine dye CV^{2+} with a covalently linked viologen group $(n = 5)$.

vectorial processes for light conversion [35,36,40,137–143].

By incorporating electron acceptors (e.g. methyl viologen molecules) in J-aggregates, light-induced charge separation could be observed [35,36,40]. By fixing the electron acceptors at a specific location in the aggregate (e.g. by using cyanine dyes with covalently bonded viologen groups as energy trap in the aggregate; see Fig. 8(b)), an even more efficient light-induced charge separation could be observed (see Fig. 9). It was assumed that exciton formation in the aggregate, which also causes a strong light-harvesting and antenna effect, is responsible for the stabilization of the charge-separated state [35,36,40,141,143–148]. The better intramolecular charge separation (open circles in Fig. 9) compared with the intermolecular process (open squares in Fig. 9) was explained by a more suitable geometrical arrangement of the linked viologen groups for electron transfer [35,36].

Owing to the high absorption coefficient of the J-band, thin aggregate films could be used for light energy conversion. Additionally, by using different J-aggregate-forming cyanine dyes [148], the whole solar spectrum could be covered. Therefore J-aggregate-based systems for conversion of solar energy seem to be very promising and will be further investigated.
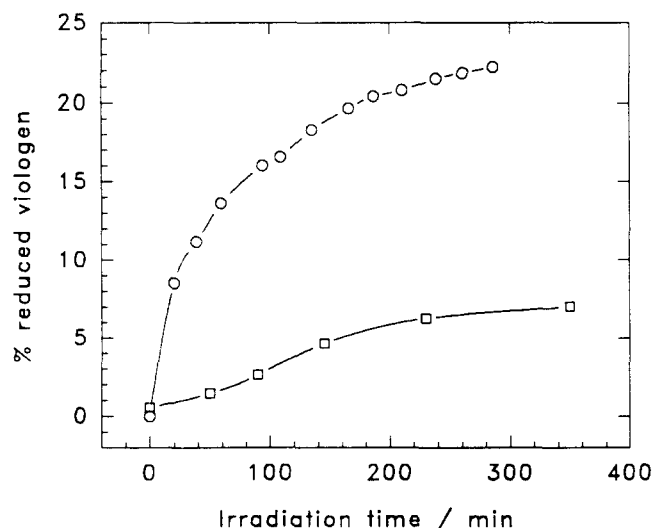
Fig. 9. Light-induced reduction of MV^{2+} (-□-) and CV^{2+} (-○-). (After Ref. [40].)

Besides kinetic problems, competing side reactions exist, usually both diminishing quantum yields and destroying the components of the system. These are discussed in the next two subsections, separately for the photosensitizer and the electron relay component.

2.2.2.2. Stability of photosensitizers

Owing to their high energy content in the excited state, photosensitizers can (easily) undergo various types of degradation processes in a water photolytic system [48]. For example, using zinc porphyrin (ZnP; S7 in Fig. 3) as the photosensitizer, a high quantum yield of H_2 can be achieved (at the beginning of the irradiation), but the ZnP is destroyed very fast, even in the absence of oxygen (see Fig. 10). Compared with ZnP, the photostability of $Ru(bpy)_3^{2+}$ (S9 in Fig. 3) is much better [48,111].
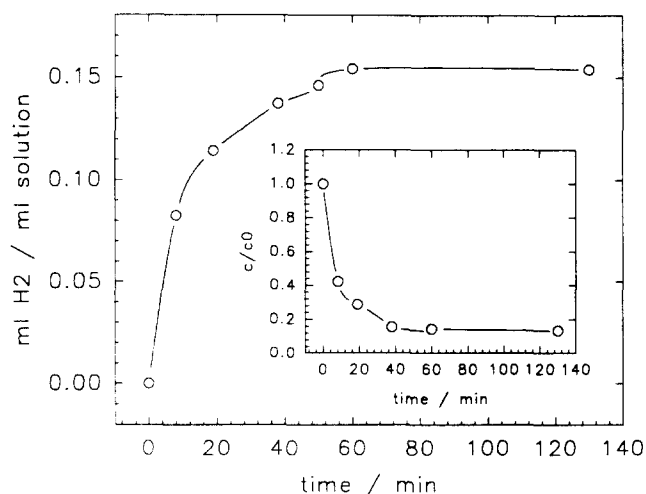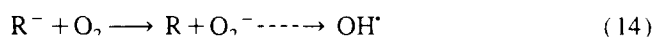

Fig. 10. H_2 formation with ZnP/MV^{2+}. Inset: degradation of ZnP as a function of irradiation time. Conditions: 3 ml (ZnP, $c_0 = 1.6 \times 10^{-4}$ mol l^{-1}; MV^{2+}, $c_0 = 1.93 \times 10^{-3}$ mol l^{-1}; EDTA, 0.05 mol l^{-1}; platinum catalyst, $c_0 = 7.4$ mg l^{-1}; acetate buffer) were irradiated with a 150 W tungsten halide lamp (400 nm cut-off and 10 cm IR water filter) [173].

The most important destruction pathway of dyes (photosensitizers) is their reaction with oxygen. Dyes possessing long-lived excited triplet states (e.g. $^3Ru(bpy)_3^{2+*}$) can undergo triplet–triplet annihilation [149–151] with oxygen, forming the highly reactive singlet oxygen, which can destroy the (organic) dye in a consecutive reaction. On the other hand, ground state reduction of oxygen can occur mediated by the reduced relay compound R^-, leading finally to OH^* radicals. The OH^* radicals are highly reactive species too:

$$S^* + R \xrightarrow{k_{O_2}} S^+ + R^- \tag{11}$$

$$R^- + O_2 \longrightarrow R + O_2^- \cdots\cdots\rightarrow OH^* \tag{14}$$

$$S/R + OH^* \longrightarrow \text{products} \tag{15}$$

Rate constants for the reaction of reduced viologens with oxygen are reported by Infelta [112] to be in the region of $k_{O_2} = 5 \times 10^9$ l mol^{-1} s^{-1}.

Additionally, various other photodegeneration pathways (occurring also in the absence of oxygen) exist, e.g. loss of a ligand L or ligand substitution in dyes based on complexes such as $Ru(bpy)_3^{2+}$ (L ≡ (bpy) or other polypyridine compound) [52–54]:

$$Ru(L)_3^{2+*} \longrightarrow Ru(L)_2^{2+} + L \tag{16}$$
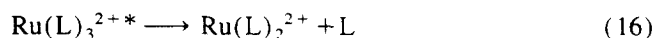
This ligand photosubstitution is described [52,53,152] as proceeding via a (thermally activated) radiationless transition from the luminescent ^3MLCT (triplet metal to ligand charge transfer) state to a distorted ^3MC (triplet metal centred) level, with subsequent competition between radiationless decay to the ground state and decomposition of the photosensitizer. This occurs via formation of an intermediate consisting of a monodentate (L) ligand [153,154]. The intermediate undergoes either loss of the ligand (with possible subsequent complexing by solvent molecules) or chelate ring closure and reformation of $Ru(L)_3^{2+}$. In order to avoid ligand substitution or ligand loss, Ru(II) cage-type complexes have been developed [53] where the bipyridine ligands are fixed together (via various types of flexible or rigid bridges [53,155–157]). Thus ligand loss is no longer possible. Owing to the rigidity of the cage system, a slowing down of the radiationless decay process with a consequent increase in lifetime and emission intensity could be achieved. On the other hand, if the cage-type ligand forces a structure with unsuitable metal–N bond distances or unfavourable coordination geometry, radiationless deactivation processes would be favoured owing to a lower-lying ^3MC level [53].

Another important problem is that the lowest excited state of most Ru(II)–polypyridine sensitizers is a triplet state, still favouring singlet oxygen formation. In order to avoid the oxidation of S or R by singlet oxygen and/or other oxygen-based, highly reactive intermediates (OH^*), photoelectrochemical systems have been discussed consisting of two separate compartments, one for H_2 evolution and the other for O_2 generation (or other oxidative processes) [158,159]. If the sensitization process occurs (only) in the (oxygen-

$$(17)$$

$$(18)$$

$$(19)$$

$$(20)$$

$$(21)$$

Scheme 3.

$$(22)$$
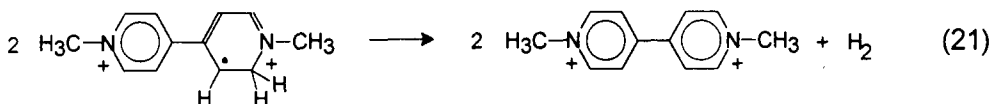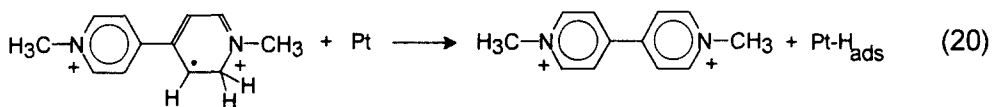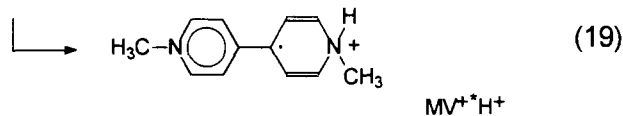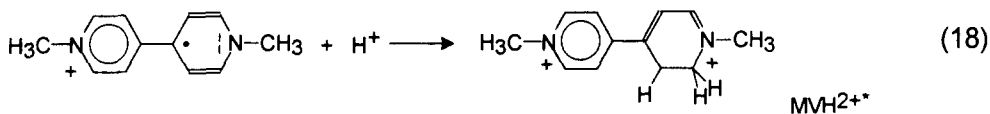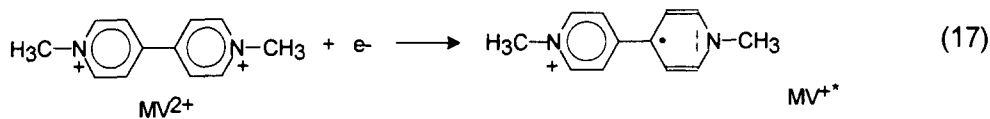
$$(23)$$
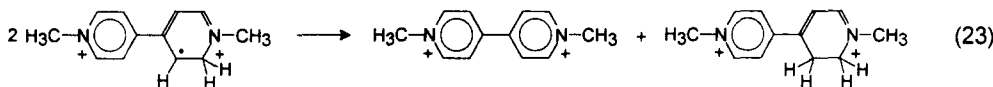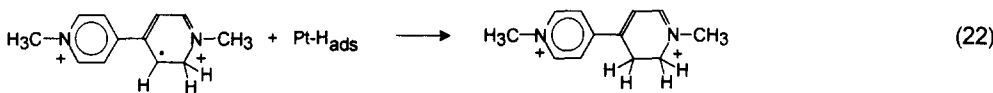
Scheme 4.

free) "H_2 compartment", the destruction of the dye by oxygen is no longer possible.

Various other attempts have been made to find more stable dyes (e.g. trinuclear ruthenium complexes or phthalocyanines [111,155–157,160]). Phthalocyanine dyes are known to be much more stable than porphyrins, but owing to their low solubility, their application is very limited. Hence further work has to be undertaken to find an ideal photosensitizer for water photolysis.

2.2.2.3. Stability of electron transfer compounds

The most common electron transfer (relay) compound is methyl viologen (MV^{2+}; see Fig. 4). This system and its analogues are unique organic substances owing to their reversible one-electron redox reaction occurring at negative redox potentials ($E° = -0.4$ V vs. normal hydrogen electrode (NHE) [82,83,161]).

However, owing to their aromatic structure, they are susceptible to hydrogenation reactions, which were first investigated by Getoff and coworkers [162–165] as well as by Mau and coworkers [79–81].

Besides the hydrogenation of MV^{2+} in the dark, occurring via attack by hydrogen atoms, an additional destruction path-

way has to be assumed because of the lower stability of viologens in water photolysis systems than one would expect. We assumed [34] that the protonation of the reduced viologen cation radical $MV^{·+}$ provides a second and even more efficient degradation pathway which is mainly responsible for the decomposition of MV^{2+} in water photolysis systems.

Based on kinetic data, a model has been developed for H_2 formation (via protonation of viologen) and for hydrogenation of the viologens [25,34] (see Scheme 3).

After reduction of the viologen dication MV^{2+} to $MV^{·+}$, Eq. (17), protonation takes place. In principle this can yield a ring (MVH^{2+}), Eq. (18), or a nitrogen adduct ($MV^{·+H+}$), Eq. (19). As a further process the abstraction of a hydrogen atom by a platinum particle (colloidal catalyst) should given an absorbed $H·$ radical ($Pt-H_{ads}$) and an undestroyed viologen MV^{2+}, Eq. (20). As second formation reaction two MVH^{2+} (or $MV^{·+}H^+$) molecules can react with each other to form hydrogen and two MV^{2+}, Eq. (21). This was confirmed by H_2 evolution experiments with MV^{2+} in catalyst (Pt)-free solutions [25].

Similarly to the formation process, the destruction of MVH^{2+} occurs via two reactions, one involving hydrogen

$$k_{dep} = 2 \times 10^4 \text{ s}^{-1} \quad (24)$$

$$k_{dep} = (6.0 \pm 0.1) \times 10^8 \text{ l / mol s} \quad (25)$$
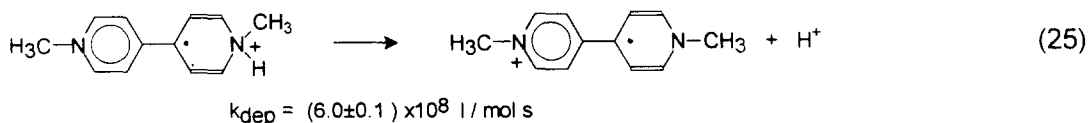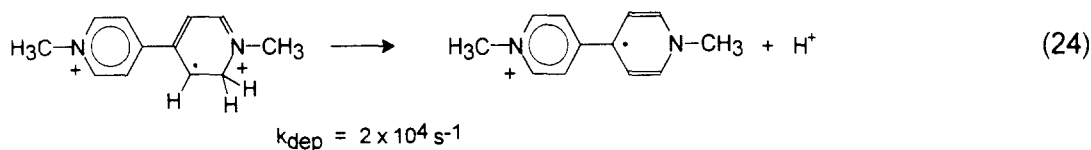
Scheme 5.

adsorbed on platinum particles (Pt–H_{ads}), Eq. (22), and the second according to Eq. (23) (see Scheme 4).

In contrast with this reaction mechanism, hydrogen evolution from reduced viologen cation radicals $MV^{\cdot+}$ in the presence of platinum particles was described by an electron pool mechanism [25,28]. In this model the platinum particle should act as a (heterogeneous) microelectrode, first obtaining electrons from $MV^{\cdot+}$ and afterwards reducing two H^+ to H_2.

Although the protonation reaction of $MV^{\cdot+}$ is evidenced [25], electron transfer from $MV^{\cdot+}$ to Pt particles can also take place. Whether electron transfer to platinum (particles or electrodes) or protonation of $MV^{\cdot+}$ is the main route for H_2 formation can be clarified by comparison of the reaction rates for the two reactions. The pK_a values for the protonation of $MV^{\cdot+}$ was determined to be $pK_a = 4 \pm 0.2$ [25]. Following pulse radiolysis experiments performed by Getoff and his group, we can obtain the reaction rate constants for the deprotonation of protonated $MVH^{\cdot2+}/MV^{\cdot+}H^+$ [164,165], with two different values depending on the species: $k_{dep} = 2 \times 10^4 \text{ s}^{-1}$ for the ring-protonated $MVH^{\cdot2+}$ and $k_{dep} = (6 \pm 0.1) \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ for the nitrogen-protonated $MV^{\cdot+}H^+$ (see Scheme 5).

From the pK_a value [25] and k_{dep} [164,165] the rate constants for the protonation reaction can be estimated to be in the range $10^8–10^{12} \text{ l mol}^{-1} \text{ s}^{-1}$. As this is much faster than electron transfer reactions to metal electrodes [159], we conclude that (at lower pH) the protonation of $MV^{\cdot+}$ is an important pathway for H_2 evolution and competes with heterogeneous electron transfer.

Besides the reduction of viologens, the attack by $OH^{\cdot}$ radicals (Eq. (15)) generated via reduction of oxygen (accord-

ing to Eq. (14)) can also cause the destruction of viologens [163]. The sensitivity of reduced viologens towards oxygen was the reason for the use of oxygen-free solutions for hydrogen evolution experiments (with a "sacrificial" electron donor according to Fig. 6(b)). However, 1,1'',1'''-trialkyl[4,2';4',4'';6',4''']quaterpyridinium trichlorides (see Fig. 11), compounds quite similar in structure to viologens, were found to be much more stable towards oxygen in their reduced state [32]. Reversible redox potentials were found to be in the same range as for MV^{2+} [37]. Hydrogen gas evolution experiments (with EDTA as the "sacrificial" electron donor) gave almost the same quantum yields in the presence of oxygen as in its absence [111]. Experiments with viologens under similar conditions showed significantly lower quantum yields in the presence of O_2.

Various attempts have been made to increase the stability of viologens, e.g. by structural modifications [34,81]. It could be shown that the introduction of substitutents in the position α to the ring N led to increased stability. For example, the 1,1'-dimethyl-2-phenyl-6-(p-tolyl)-4,4'-bipyridinium dication (R1; see Fig. 4) has a twofold higher turn-over number than MV^{2+} [34]. However, for practical applications, long-term stability is needed, which most probably cannot be achieved by viologen compounds.

Besides viologens, there are other classes of substances which are more promising: cobalt sepulchrate (see Fig. 5) and related compounds as well as Rh or Co complexes [48,55,89,166], which can act as homogeneous catalysts (e.g. Wilkinson catalysts [90–92,167,168]). Among these electron transfer substances and catalysts, cobalt sepulchrate seems to be the best choice owing to its high stability towards hydrogenation and its low reactivity towards oxygen ($k = 44 \text{ l mol}^{-1} \text{ s}^{-1}$ [169–172] compared with $k_{O_2} = (2–8) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ for viologens [112]). In long-term experiments on light-induced hydrogen formation, cobalt sepulchrate was shown not to be destroyed [93,173,174]. Consequently, in cobalt sepulchrate we have a very promising candidate for the function of the electron relay substance.

3. Summary

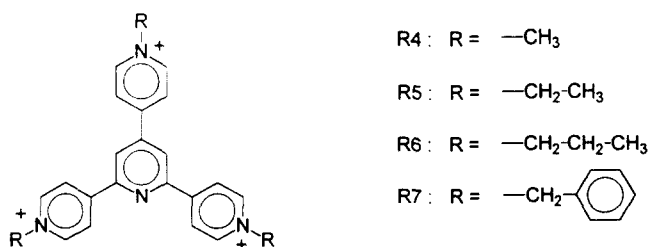Two systems for the conversion of light energy have been described, one based on light-induced hydride transfer and

R4 : R = —CH₃

R5 : R = —CH₂-CH₃

R6 : R = —CH₂-CH₂-CH₃

R7 : R = —CH₂-⟨phenyl⟩

Fig. 11. 1,1'',1'''-Trialkyl[4,2';4',4'';6',4''']quaterpyridinium trichlorides R4–R7.

the other based on light-induced electron transfer processes. It was shown that using (poly)aromatic keto compounds as photosensitizer, light-induced H_2 formation with simultaneous oxidation of alcohols can occur only when applying UV light irradiation. Although pyrrolizinone derivatives with absorption in the visible region have been found, no visible-light-induced H_2 evolution was possible.

Systems based on light-induced electron transfer can successfully be used for H_2 formation when a ''sacrificial'' electron donor (e.g. EDTA) is consumed. In the case of cyclic water splitting based on diffusion-controlled reactions, kinetic problems diminish the quantum yield. Applying the Marcus theory, rate constants of forward and back electron transfer can be compared by comparing the standard free enthalpies of reactions. As a result of the evaluation of electron transfer in terms of thermodynamic driving forces it was concluded that back reactions are usually faster than forward reactions. Well-organized systems (e.g. J-aggregates), as in nature, with spatial charge separation and applying vectorial processes are proposed as one possibility to overcome these difficulties.

The stability of photosensitizers and electron relay compounds, affected by several side and consecutive reactions, is another major problem. While photosensitizers are mainly destroyed via oxidative processes involving highly reactive species such as singlet oxygen or OH^- radicals, the main destruction pathway for viologens is hydrogenation, which also can proceed via protonation of reduced viologens. Cobalt sepulchrate, possessing a high stability towards hydrogenation and a low reactivity towards oxygen, is proposed as an ideal electron relay compound for light-induced H_2 formation. However, considerable and concerted efforts are required to develop a system for cyclic water splitting with high quantum yields.

Acknowledgements

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