

PHOTOCHEMICAL WATER CLEAVAGE: A SIMPLE KINETIC ANALYSIS

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Summary

We present a simple kinetic model for cyclic water cleavage by a system containing an aqueous solution of a sensitizer, an electron acceptor and two specific catalysts. We illustrate quantitatively how the hydrogen production rate is affected by various parameters such as the concentrations of the solutes, the pH of the solution, the partial pressure of oxygen and hydrogen, the efficiencies of the catalysts, the irradiation intensity and the redox potential of the acceptor. The maximum achievable Φ_{H_2} is calculated for various operating conditions.

1. Introduction

Conversion of solar energy into chemical energy by photochemical water cleavage is the object of intensive investigations [1]. The final goal is to achieve the reaction



where a number of visible light photons are used to decompose a water molecule.

In one of the simplest schemes, which we shall investigate further here, an aqueous solution at room temperature contains a sensitizer S and an electron acceptor A. Upon photoexcitation the sensitizer acts towards A as an electron donor according to



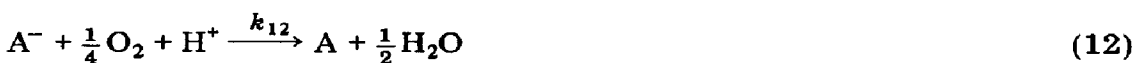
For a suitable choice of S and A reaction (2) can be followed by



and the overall reaction is reaction (1). The choice of S and A is crucial. Destructive side reactions of A, A⁻, S and S⁺ must be non-existent. The redox potentials of the couples S|S⁺ and A⁻|A must be appropriate for reactions (3) and (4) to be thermodynamically favourable. The rates of the desired reactions can be enhanced by using specific catalysts. We have demonstrated elsewhere that some unwanted reactions can be slowed down by using microheterogeneous systems such as micelles [2]. Undesirable reactions which consume S⁺ and A⁻ must be minimized. Our aim in the present work is to undertake a simple kinetic analysis of such systems. We limit our investigation to systems that operate at room temperature where the sensitizer S is the ruthenium trisbipyridyl ion (Ru(bpy)₃²⁺). Varying the redox potential of S or the operating temperature would not enhance any essential features, even though the importance of the choice of S or of the operating temperature should not of course be overlooked in any practical system. We obtain quantitative information on the maximum achievable conversion yield and on the effects on the rate of decomposition of the concentrations of the various solutes, the pH, the partial pressures of oxygen and hydrogen, the efficiencies of the catalysts and the redox potential of the A⁻|A system. We also show that there is an irradiation intensity threshold below which cyclic water cleavage cannot take place.

2. Kinetic model

As a working hypothesis, we have assumed that the following reactions give a reasonable description of the type of system under investigation (for simplicity we represent Ru(bpy)₃²⁺ by S):



Reactions (5) - (9) are self-explanatory. k_f describes the natural decay of the excited state. k_{O_2} and k_q represent the quenching of S^* by oxygen and by the acceptor respectively. k_b is the rate for the back electron transfer. Φ is the maximum yield for electron transfer quenching. The equilibrium constants K_{10} and K_{11} can be obtained from the known redox potentials of the system involved (see Appendix A). In a recent analysis [3] of this type of system, reactions (8') and (12) were not included while reactions (10) and (11) were assumed to be irreversible. Reaction (8') takes into account the fact that the quenching does not necessarily lead to electron transfer with unit efficiency. In the present study the reversibility of reactions (10) and (11) provides the thermodynamic limit beyond which they cannot possibly take place. Reactions (10) and (11) are of course a simplification of the processes which are taking place. To produce hydrogen (or oxygen) a catalyst particle must acquire a charge which brings it to a suitable potential to achieve reduction (or oxidation) of water. When a photostationary state is established the charge transfer rate between A^- (or S^+) and a catalyst particle will be affected by the potential of the particle. If a catalyst is efficient (low overpotential, rapid gas evolution, low charge accumulation per particle) the rate-limiting step will be the charge transfer between the radical ion and the particle which may reach the diffusion-controlled limit. If an inefficient catalyst (large overpotential, slow gas evolution, large charge accumulation per particle) is used for the same S|A couple, the charge transfer rate at the photostationary state will of course be lowered substantially. The catalyst efficiencies can thus be reflected in the values selected for the forward rates of reactions (10) and (11). With these restrictions kept in mind, reactions (10) and (11) provide an adequate description for our present purpose.

Finally, the oxidation of reduced acceptors such as methyl viologen (MV^{2+}), schematically described here by reaction (12) (see below for more detailed kinetic considerations), is known to occur at rates close to the diffusion-controlled limit [4] and therefore cannot be ignored in the description of systems where oxygen is not removed immediately after its formation.

From this reaction scheme we write the differential time laws relative to the various species:

$$\frac{d[S]}{dt} = -R[S] + k_f[S^*] + (1 - \Phi)k_q[S^*][A] + k_b[S^+][A^-] + k_{10}[S^+] - k_{-10}[S][H^+][O_2]^{1/4} + k_{O_2}[O_2][S^*] \quad (13)$$

$$\frac{d[S^*]}{dt} = R[S] - k_f[S^*] - k_q[S^*][A] - k_{O_2}[O_2][S^*] \quad (14)$$

$$\frac{d[A^-]}{dt} = \Phi k_q[S^*][A] - k_b[S^+][A^-] - k_{11}[A^-] - k_{12}[O_2][A^-] + k_{-11}[A][H_2]^{1/2}[OH^-] \quad (15)$$

Additionally the total amount of sensitizer or acceptor under all forms is constant:

$$[S] + [S^*] + [S^+] = C_1$$

$$[A] + [A^-] = C_2$$

In the above we assume that the formation rate of the excited state S^* is proportional to the actual sensitizer concentration. The irradiation intensity R thus contains such information as the photon flux and the quantum yield for formation of S^* which we do not wish to include explicitly here. This also implies that we are only considering a volume of solution which is uniformly irradiated. The variations of the irradiation rate along the absorption path would have to be taken into account in a practical realization since it is expected that attempts to absorb the largest possible fraction of the incident photon flux would normally be made. We shall come back to this point later.

The terms in eqns. (13) - (15) involving k_f , k_q and k_b require no further explanation.

It is known that in a homogeneous aqueous solution equilibrium (10) may never be achieved. Furthermore, depending upon the pH conditions, other reactions can occur which lead to the consumption of S^+ without production of oxygen [5].

In the presence of an appropriate catalyst, equilibrium (10) may be obtained. For a practical system able to perform sustained water cleavage, it is necessary to use a specific catalyst, *i.e.* a catalyst in the presence of which no reaction of any of the other redox systems present such as $H^+|H_2$ and $A|A^-$ can take place. Thus catalytic combination of oxygen with hydrogen cannot take place on such a catalyst. The development of such catalysts is the object of a significant number of studies [6 - 11]. In the above model, we consider only the case where the catalysts are present in the form of small particles randomly distributed throughout the solution. Furthermore, we have assumed that with a specific catalyst at constant concentration, the rate of reaction (10) in the forward direction follows first-order kinetics with rate $k_{10}[S^+]$. This can be the case if the rate-limiting step is the reduction of S^+ by its reaction with the catalyst particles which in turn react with H_2O or OH^- to produce oxygen. It is clear that the rate k_{10} will depend upon the catalyst, its concentration and possibly other factors such as pH, ionic strength, temperature etc.

It is almost impossible to obtain a rate for reaction (10) in the reverse direction unless a detailed mechanistic investigation of the system can be undertaken. Our main interest, however, resides in the continuous photolysis of the system. Under constant illumination a true photostationary state can be attained if the material input to the system is adjusted to its output. If such a system is successfully decomposing water into its elements, water must be added to the system at a rate corresponding to the formation of hydrogen and oxygen, the partial pressures of these two gases being kept

constant. If the irradiation rate becomes too small, equilibria (10) and (11) and reaction (9) will correspond to a catalytic combination of H_2 and O_2 (as we shall see below) and the input to the system will become hydrogen and oxygen while the output will be water. As an approximation to the rate of reaction (10) in the reverse direction, we use the rate obtained from the equilibrium constant, the forward rate and the concentration of the various species: $k_{-10} = k_{10}/K_{10}$. The same type of considerations apply to equilibrium (11). A specific catalyst for the $\text{A}^-|\text{A}$ system, which is different from the previous specific catalyst, must be present. The pseudo-first-order reaction of A^- with the catalyst is assumed to be the rate-limiting step in the water reduction process. Reaction of the catalyst with H_2O or H^+ subsequently completes reaction (11). The rate for reaction (11) in the reverse direction is again estimated from the forward rate, the equilibrium constant and the various concentrations needed: $k_{-11} = k_{11}/K_{11}$. We should mention here that if k_{10} and k_{11} are assumed to be independent of pH, then the pH dependences of the thermodynamics of the system are found in k_{-10} and k_{-11} .

Reaction (12) deals with the possible oxidation of the A^- species by the oxygen produced. When A is a bipyridylum dication (BP^{2+}) the primary redox step is



where $k_{16} \approx (2 - 8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for quite a significant span in redox potential [3]. Subsequent reactions of O_2^- may result in the formation and build-up in concentration of other species, *i.e.* O_2^{2-} , H_2O_2 etc. It is clear from the point of view of the redox balance of reaction (12) that each O_2^- formed via reaction (16) may result in the oxidation of at most another three BP^+ radicals. When the steady state is reached the actual rate k_{12} will thus be about $(1 - 4) \times k_{16}$. It is quite clear that reaction (12) represents an oversimplification of the actual phenomena. However, it allows us to perform a more general analysis than would be possible with a more detailed scheme that would only be applicable to one S|A couple.

We also assume that the reaction



does not occur. This is known to be the case for $\text{Ru}(\text{bpy})_3^{3+}$ [12]. Of course, the specific catalysts of equilibria (10) and (11) must not catalyse this reaction.

3. Steady state photolysis considerations

Our aim is to find the conditions under which as large a fraction as possible of the light energy input to the system is used to produce hydrogen and oxygen. It is clear that the absorbance characteristics of the sensitizer and the quantum yield for the formation of the excited state will play an

important role. This, however, is a trivial problem which we do not wish to address here.

Let us consider a system under continuous irradiation which has achieved a photostationary state. All concentrations must remain constant. Thus if the system is splitting water successfully, hydrogen and oxygen must be removed at the rate at which they are produced and H_2O must be added to compensate for the dissociation. For such a system the left-hand side of eqns. (13) - (15) is zero. For selected values of the concentrations of the sensitizer S, the acceptor A and a chosen pH, eqns. (13) - (15) together with the fact that the total amount of sensitizer and acceptor under all forms is constant allow the determination via a numerical solution of the concentrations of all the species present in the solution. It should be noted here that, in view of the stoichiometry of the redox reactions, the pH of the solution of such a photostationary system remains constant and the overall reaction is reaction (5), *i.e.* the hydrogen production rate is always twice that of oxygen. By simple inspection of the kinetic scheme we can write the formation rate of oxygen and hydrogen for such a photostationary system:

$$r_{O_2} = \frac{1}{4} \left(k_{10}[S^+] - \frac{k_{10}}{K_{10}} [S^+][H^+][O_2]^{1/4} - k_{12}[O_2][A^-] \right) \quad (18)$$

$$r_{H_2} = \frac{1}{2} \left(k_{11}[A^-] - \frac{k_{11}}{K_{11}} [A][OH^-][H_2]^{1/2} \right) \quad (19)$$

With these conventions a negative rate for formation indicates gas consumption. It is now a simple matter to examine the behaviour of such a system and the effects of the various parameters.

4. Results

The dependence of the behaviour of such a system on all the parameters is rather complicated. We restrict our presentation here to the rate of evolution (or consumption) of hydrogen from solutions under various conditions, while throughout this paper a number of parameters have been kept constant for simplicity. The actual values used are given in Table 1. The rate parameters and the redox potential $S^+|S$ correspond to the use of $Ru(bpy)_3^{2+}$ as a sensitizer. The value for the maximum electron transfer quantum yield $\Phi = 0.3$ [13] is that obtained when A is MV^{2+} . Prior to the discussion of our results, we shall justify the typical numerical values selected for the parameters that are varied here.

4.1. Irradiation

The solution is in equilibrium with the atmosphere above it where the partial pressure of hydrogen is always twice that of oxygen. This situation results from water decomposition. For a number of calculations we selected a value of 5 s^{-1} for the irradiation intensity R which corresponds to a pro-

TABLE 1

Curve labels, hydrogen yields and corresponding parameters

Fig- ure	Curve label ^a	Maxi- mum Φ_{H_2} (%)	k_{10} (s^{-1})	k_{11} (s^{-1})	k_{12} ($M^{-1} s^{-1}$)	[A] ($mol\ l^{-1}$)	p_{O_2} (atm)	pH	R (s^{-1})	$A^- A$ redox potential (V)
1	2	0.180	1000	6000	1×10^9	Var.	0.333	2	5	-0.640
	2'	0.030	1000	6000	4×10^9	Var.	0.333	2	5	-0.640
	3	0.080	1000	6000	1×10^9	Var.	0.333	3	5	-0.640
	3'	6.000	Inf.	Inf.	1×10^9	Var.	0.333	3	5	-0.640
	4	—	1000	6000	1×10^9	Var.	0.333	4	5	-0.640
	4'	0.200	1000	6000	1×10^9	Var.	0.100	4	5	-0.640
2	2d	0.040	1000	6000	1×10^9	Var.	0.033	2	5	-0.445
	2e	0.200	Inf.	Inf.	1×10^9	Var.	0.033	2	5	-0.445
	3c	0.800	1000	6000	1×10^9	Var.	0.033	3	5	-0.550
	3d	—	1000	6000	1×10^9	Var.	0.033	3	5	-0.445
	4a	1.400	1000	6000	1×10^9	Var.	0.033	4	5	-0.640
	4b	10.000	Inf.	Inf.	1×10^9	Var.	0.033	4	5	-0.640
4c	—	1000	6000	1×10^9	Var.	0.033	4	5	-0.550	
3	1	7.000	Inf.	Inf.	1×10^9	Var.	0.033	3	5	-0.550
	2	0.800	1000	6000	1×10^9	Var.	0.033	3	5	-0.550
	2a	0.080	1000	600	1×10^9	Var.	0.033	3	5	-0.550
	2b	0.010	1000	60	1×10^9	Var.	0.033	3	5	-0.550
	2c	0.140	1	6000	1×10^9	Var.	0.033	3	5	-0.550
4	2	0.080	1000	6000	1×10^9	2×10^{-3}	0.333	2	Var.	-0.640
	3	0.080	1000	6000	1×10^9	2×10^{-3}	0.333	3	Var.	-0.640
	3'	0.333	1000	6000	1×10^9	2×10^{-3}	0.100	3	Var.	-0.640
	4	0.080	1000	6000	1×10^9	2×10^{-3}	0.333	4	Var.	-0.640
5	2a	6.000	1000	6000	1×10^7	2×10^{-3}	Var.	2	5	-0.640
	3c	6.000	1000	6000	1×10^9	2×10^{-3}	Var.	3	5	-0.445
	3d	6.000	1000	6000	1×10^9	2×10^{-3}	Var.	3	50	-0.445
	4a	6.000	1000	6000	1×10^9	2×10^{-3}	Var.	4	5	-0.640
	4b	6.000	1000	6000	1×10^9	2×10^{-3}	Var.	4	5	-0.550
	4c	6.000	1000	6000	1×10^9	2×10^{-3}	Var.	4	5	-0.445
6	1	4.000	Inf.	Inf.	1×10^9	2×10^{-3}	0.333	Var.	5	-0.640
	1a	0.060	1000	6000	1×10^9	2×10^{-3}	0.333	Var.	5	-0.640
	1b	0.500	1000	6000	1×10^8	2×10^{-3}	0.333	Var.	5	-0.640
	1c	2.400	1000	6000	1×10^7	2×10^{-3}	0.333	Var.	5	-0.640
	2	0.040	1000	6000	1×10^9	2×10^{-3}	0.333	Var.	5	-0.550
	3	—	1000	6000	1×10^9	2×10^{-3}	0.333	Var.	5	-0.445

In all of the results presented we used the following: $k_f = 1.6 \times 10^6 s^{-1}$; $k_q = 5 \times 10^8 M^{-1} s^{-1}$; $k_b = 2.4 \times 10^9 M^{-1} s^{-1}$; $k_{O_2} = 2 \times 10^9 M^{-1} s^{-1}$; $[S] = 1 \times 10^{-4} M$; $E_{S^+|S} = 1.260 V$; $\Phi = 0.3$; $p_{H_2} = 2p_{O_2}$.

In all the figures hydrogen and oxygen consumption is indicated by a sinusoidal modulation superimposed on the calculated curve.

Inf., the rate used is infinite; var., the variable selected in that particular figure.

^aIn Figs. 1, 2, 4 and 5 the number on the curve also corresponds to the selected pH.

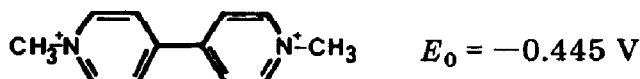
duction rate of S^* of about $5 \times 10^{-4} \text{ M s}^{-1}$ (in cases where $[S^+]$ and $[S^*]$ are negligible). This corresponds roughly to the average rate of production of the excited state in a $10^{-4} \text{ M Ru(bpy)}_3^{2+}$ solution 1 cm thick irradiated with the output of a 450 W xenon arc unfocused in the wavelength region 400 - 550 nm. The production rate of S^* obtained by irradiating the same solution with sunlight can be expected to be smaller by a factor of 10 - 50.

4.2. Catalyst efficiencies

We can obtain an estimate for k_{11} as $4\pi rDN[\text{cat}]_{\text{part}}$ where r is the radius of the catalyst particles (about 20 - 30 Å), D is the diffusion coefficient of the radical ion (about $10^{-5} \text{ cm}^2 \text{ s}^{-1}$), N is Avogadro's number and $[\text{cat}]_{\text{part}}$ is the particle concentration of the catalyst. For platinum spherical particles 20 Å in diameter [11] (21.4 g cm^{-3}), a pseudo-first-order rate k_{11} of 5600 s^{-1} for a platinum weight concentration of 40 mg l^{-1} is found. Hence we selected 6000 s^{-1} as a typical value. The same type of consideration allows the determination of an estimate for the charge transfer reaction between S^+ and RuO_2 catalyst particles, for example, on a TiO_2 support [14]. A value of 1000 s^{-1} for k_{10} is a realistic estimate which corresponds to experimental values. As we shall see, however, the behaviour of the system seems rather insensitive in general to this catalyst efficiency.

4.3. Redox potential of A

We selected three redox potentials which correspond to the following bipyridylum ions:



I, MV^{2+}



II



III

All these ions are effective quenchers of $\{\text{Ru(bpy)}_3^{2+}\}^*$ even though the quenching rate for III is slightly smaller than the k_q rate used here. These types of redox potential still allow a sufficient drive from the $S^+|S^*$ system ($E_{S^+|S^*} \approx -0.860 \text{ V}$) [15]. We do not know the actual maximum electron transfer quantum yields for II and III.

4.4. Other parameters

The rate k_{12} was taken as $10^9 \text{ M}^{-1} \text{ s}^{-1}$ most of the time. This corresponds to the rate of reaction (16) for compound III [4] which, of the three compounds selected here, is the most reactive towards oxygen. The actual rate used to take into account the build-up of secondary products could be up to four times as large but would depend on the actual chemistry involved, as discussed in the presentation of the kinetic model.

An oxygen pressure of 0.333 atm corresponds to gas production at 1 atm pressure. No additional work is required to recover the products.

Figures 1 - 6 present a variety of results and the corresponding parameters are shown in Table 1. Curves with a sinusoidal curve superimposed indicate consumption rather than production of hydrogen. All of the parameters used are summarized in Table 1. The maximum hydrogen quantum yield Φ_{H_2} , obtainable is also reported where applicable.

4.4.1. General impression (Fig. 1)

For the conditions of curve 2 a maximum H_2 production rate of $9 \times 10^{-7} \text{ M s}^{-1}$ is achieved ($(\Phi_{\text{H}_2})_{\text{max}} = 0.18\%$). Curve 2' shows how the maximum production rate is reduced to $1.5 \times 10^{-7} \text{ M s}^{-1}$ when the reaction rate of A^- with oxygen is increased by a factor of 4. When the pH is increased from 2 to 3 the maximum production rate decreases here by a factor of 2 and the optimal concentration of A is changed. It should be noted that if the catalysts were perfect (infinite rates for establishing equilibria (10) and (11)) then the maximum rate would be 75 times larger ($3 \times 10^{-5} \text{ M s}^{-1}$) (curves 3 and 3'). Too high a concentration of A brings about an increase in quenching that is insufficient to compensate the displacement to the left of equilibrium (11) and results in a system which consumes hydrogen and oxygen (curves 3 and 3'). When the pH is increased to 4 the system is no longer able to produce hydrogen at any concentration of A. As expected, however, lowering the working pressure to 0.1 atm of O_2 results in a production rate of $2 \times 10^{-6} \text{ M s}^{-1}$ (curve 4'). Systems that work under reduced pressure and where the reaction products could be periodically pumped out might turn out to be viable.

4.4.2. Effect of the redox potential of $\text{A}^-|\text{A}$ (Fig. 2)

Having noted the favourable effect of a reduced pressure on the rate of production of hydrogen we selected a pressure of 0.033 atm of O_2 and compared the efficiencies of acceptors with various redox potentials. We see that at pH 2 when A is MV^{2+} hydrogen is produced at a maximum rate of about $2 \times 10^{-7} \text{ M s}^{-1}$ and at a fairly low A concentration (curve 2d; curve 2e is for perfect catalysts). At pH 3, however, no production can be obtained with this acceptor (curve 3d) but the use of compound II leads to production with a maximum rate of about $4 \times 10^{-6} \text{ M s}^{-1}$ (curve 3c). At pH 4 the use of compound III leads to an even higher production rate (curve 4a; curve 4b is for perfect catalysts) but at this pH compound II can no longer produce hydrogen (curve 4c). These findings reflect the fact that equilibrium (11) is

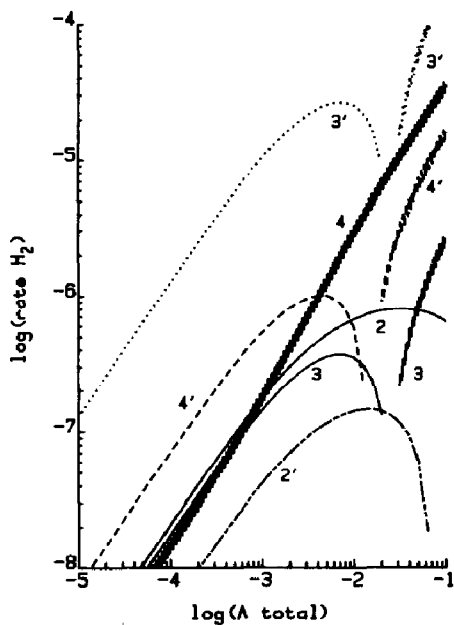


Fig. 1. Rate of production of hydrogen ($M s^{-1}$) as a function of $[A]$; the parameters are the efficiencies of the catalysts, k_{12} , the oxygen pressure and the pH (see Table 1).

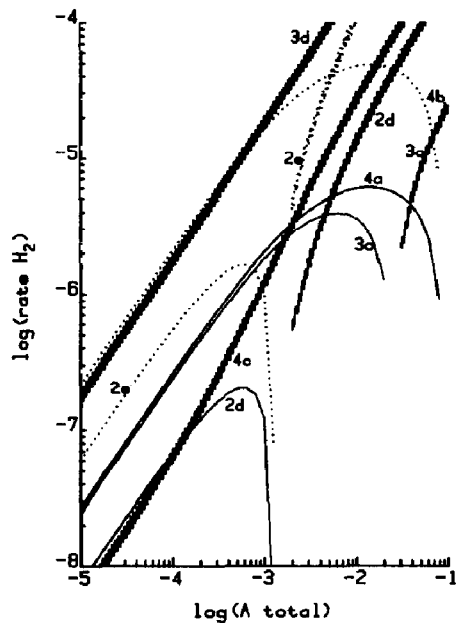


Fig. 2. Rate of production of hydrogen ($M s^{-1}$) as a function of $[A]$; the parameters are the efficiencies of the catalysts, the pH and the $A^-|A$ redox potential (see Table 1).

shifted to the right as A^- ions become more reducing. At a given pH the concentration of A^- in the solution will tend to decrease as the redox potential is decreased and reaction (12) will occur to a lesser extent. It is important to note that at this rather low pressure MV^{2+} cannot cleave water in a sustained way at pH 3 or above. We shall return to this point in the general discussion.

4.4.3. Effect of catalyst efficiencies (Fig. 3)

We now turn to the effect of the catalyst efficiencies. This is done for a particular system as reported in Table 1. We see that a decrease in the pseudo-first-order rate constant k_{11} of A^- with its catalyst by a factor of 10 results in a similar decrease in the hydrogen production rate. That this should be the case is quite understandable. The faster reaction (11) can occur in the forward direction, the lower will be the concentration of A^- and the less probable will be the occurrence of reaction (12). In contrast, a decrease in the pseudo-first-order rate constant k_{10} of S^+ with its catalyst by a factor of 1000 results only in a comparatively small decrease in the hydrogen production rate. This is due to the fact that reaction (17) does not occur. The system may be more sensitive to the magnitude of k_{10} under other operating conditions.

4.4.4. Effect of the irradiation intensity (Fig. 4)

We now turn to the importance of the irradiation intensity. It is clear that when properly catalysed such a system, if not irradiated, may lead to the catalytic combination of hydrogen and oxygen via equilibria (10) and (11) and reaction (9). Thus there will exist a minimum irradiation intensity below which production will not occur. With compound III as the acceptor, we compared the behaviour of the system at different pH values and as a function of the irradiation intensity R . The irradiation threshold increases drastically with pH. This is important since it shows that only a carefully selected system can work under given irradiation conditions. Moreover, it is noticeable that just beyond threshold the increase in the rate of production is superlinear (the slope of the log-log graph is greater than unity) and that for all pH values (2 - 4) at sufficiently high irradiation rates these three systems reach the same limit. It may be interesting in certain cases to concentrate the light and thus to be able to operate at a higher pH with almost the same conversion efficiency in order, for example, to take advantage of different properties of a catalyst at different pH values. We should mention here that it is essential that the lowest irradiation rate in the system be larger than the threshold production rate. Otherwise hydrogen and oxygen produced in a region where the irradiation intensity is high might be consumed in a region where it is low. This shows that in a practical system the total incident photon flux cannot be absorbed.

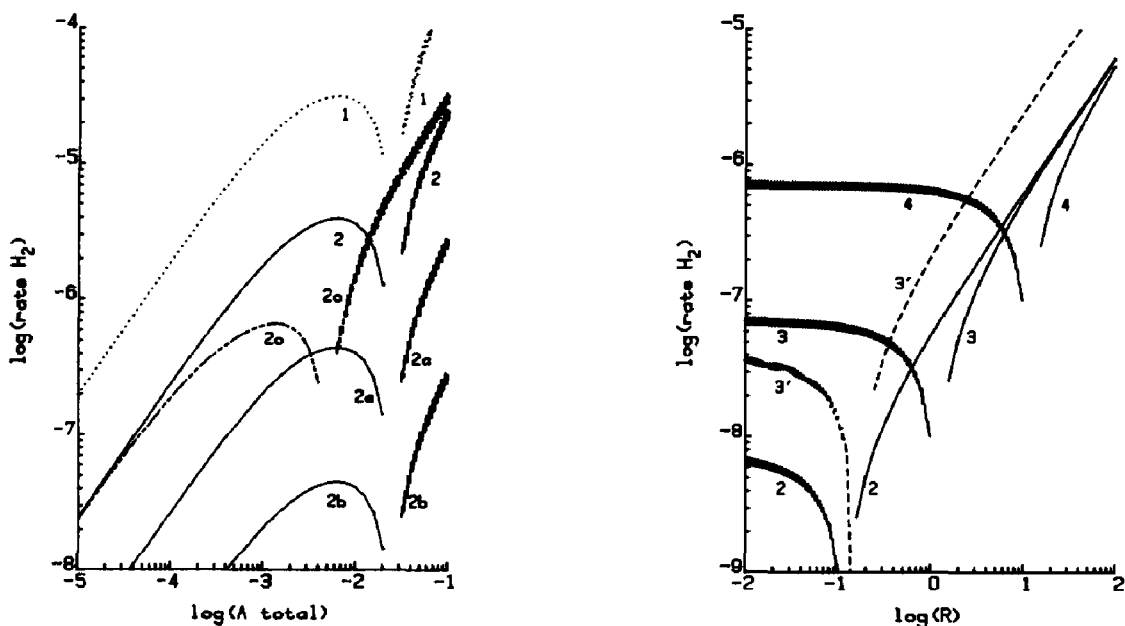


Fig. 3. Rate of production of hydrogen ($M s^{-1}$) as a function of $[A]$; the parameters are the efficiencies of the catalysts (see Table 1).

Fig. 4. Rate of production of hydrogen ($M s^{-1}$) as a function of the irradiation intensity; the parameters are the oxygen pressure and the pH (see Table 1).

4.4.5. Effect of the total pressure (Fig. 5)

We have already shown the importance of the partial pressure of the gases above the solution. For the three redox potentials selected here, curves 4a, 4b and 4c show how a marked drop in the production rate occurs when the partial pressure of oxygen increases above the solution. A system using MV^{2+} will stop producing hydrogen under a very small oxygen pressure. It is clear that acceptors with a lower $A^-|A$ potential will produce hydrogen and oxygen at a faster rate and under higher pressures. We also see that a reduction in the pH should allow the system to operate under higher oxygen pressures (curve 3c) and that if the irradiation rate is also higher the improvement is even greater (curve 3d) since at a given pressure the conversion efficiency can be better.

A solution with different A concentration and pH conditions would allow a system using compound III to produce the gases under 1 atm pressure ($p_{O_2} = 0.333$ atm). The effect of a lower reactivity of A^- towards oxygen ($k_{12} = 10^7$ s $^{-1}$) is illustrated in curve 2a where we can see that when p_{O_2} is 0.333 atm the hydrogen production rate is 1.4×10^{-5} M s $^{-1}$ which corresponds to a Φ_{H_2} of 2.8%. A better selection of the A concentration (about 10^{-1} M) would lead to an even better yield of 7%. For this particular set of parameters, this optimum yield remains the same for an irradiation intensity 100 times smaller (but this is not true if A^- is more reactive towards oxygen).

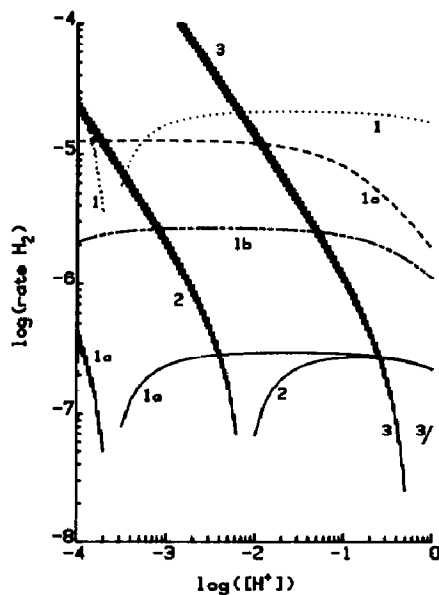
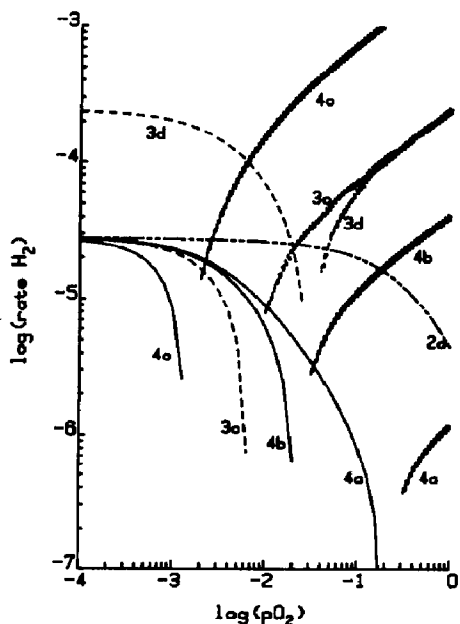


Fig. 5. Rate of production of hydrogen (M s $^{-1}$) as a function of oxygen pressure; the parameters are k_{12} , the pH, the irradiation intensity and the $A^-|A$ redox potential (see Table 1).

Fig. 6. Rate of production of hydrogen (M s $^{-1}$) as a function of the pH; the parameters are the efficiencies of the catalysts, k_{12} and the $A^-|A$ redox potential (see Table 1).

4.4.6. Effect of pH (Fig. 6)

We display here the effect of pH value. A large pH range is acceptable for compound III to produce hydrogen ($p_{O_2} = 0.333$ atm) but the finite rate of the catalysts leads to a large loss in efficiency (curves 1 and 1a). A decrease in the reaction rate k_{12} leads to a corresponding increase in the production rate of hydrogen (curves 1b and 1c) which in this case reduces the effect of the lack of efficiency of the catalyst. Finally, if the redox potential of $A^-|A$ is higher then the system can only work at lower pH (curve 2 for compound II and curve 3 for MV^{2+}). This exemplifies again the inability from a thermodynamic point of view of a system ($Ru(bpy)_3^{2+}$, MV^{2+}) to achieve water cleavage successfully.

5. Discussion

The present results illustrate the importance of some of the parameters in this type of system. We believe that it is clearly demonstrated that within the present assumptions a system with $Ru(bpy)_3^{2+}$ as a sensitizer and MV^{2+} as an acceptor is unable to achieve sustained water cleavage unless the oxygen pressure is maintained at an extremely low level.

For a logical interpretation of the successful results that have been obtained to date, more sophisticated mechanisms than those that are presented here or that have been invoked are needed [6 - 11]. We do not want to attempt to give a speculative list of all of the possibilities here. However, possible reasons are the adsorption of oxygen by one of the catalysts (or the supports) and local heat effects on a catalyst particle and in its vicinity which have a local effect on the thermodynamic properties.

We have shown that the pH region usually selected (4.5 - 5) appears inadequate from a thermodynamic point of view. It is clear, however, that catalyst efficiencies may vary enormously as a function of pH. Such variations have not been taken into account here. Detailed modelling of an actual system would be necessary to take into account ionic strength effects on the various reaction rates or parameters which have not been varied here.

It is obvious that acceptors with a lower redox potential than $MV^{2+}|MV^+$ should be investigated. The two compounds mentioned here might prove inadequate owing to unwanted side reactions or the lack of reactivity in the presence of a specific catalyst. Other acceptors similar to those proposed here are known to have the necessary capabilities [16]. Interestingly enough, their turnover number increases drastically when the pH is decreased. This would favour the development of a system operating at a somewhat lower pH.

The increased stability of $Ru(bpy)_3^{3+}$ at lower pH values is also favourable to such a system since it is well known that the natural lifetime in the absence of a catalyst is much longer at lower pH values and that unwanted reduction of $Ru(bpy)_3^{3+}$ is less likely to occur. The activity in a lower pH region of the catalysts used at present should be ascertained.

In view of the favourable effect obtained when the irradiation intensity is increased, it may well be beneficial to concentrate natural light or to use a higher concentration of sensitizer, the absorbed energy then being deposited in a somewhat smaller volume of solution. The structure of the irradiation vessel should be modified accordingly so as to make certain, as mentioned previously, that the irradiation intensity is higher than threshold everywhere. Each step requires careful optimization. Of course, the highest possible quantum yield for electron transfer is desirable. In certain systems quantum yields close to unity have been observed for electron transfer [17]. The acceptor must provide a highly reducing species but yet be as insensitive as possible to oxygen. Some of these requirements seem hard to reconcile. The optimal quantum yield Φ_{H_2} of 7% for operation under 1 atm total pressure when $k_{12} = 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ is reduced to 0.16% when $k_{12} = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Φ_{H_2} is increased tenfold to 1.6% if the total working pressure is reduced to 0.1 atm. Periodic evacuation of the products may be a practical way of operating such a system under reduced pressure.

The results obtained where the catalysts increase the rate of attainment of equilibria (10) and (11) infinitely are a definite encouragement in the attempts to find structurally organized systems such as micelles, vesicles etc. where the reduced species A^- does not have to diffuse to the catalyst but is already confined in its vicinity. Such systems would, of course, require specific modelling.

6. Conclusion

We have illustrated here from a kinetic and thermodynamic point of view some of the possibilities offered for cyclic water cleavage. It is clear that the choice of the sensitizer and the acceptor must be made wisely. It seems that the characteristics of $\text{Ru}(\text{bpy})_3^{2+}$ for S are adequate. The $\text{S}^+|\text{S}$ system is powerful enough to oxidize water even in rather acid media, while the $\text{S}^*|\text{S}^+$ system is sufficiently reductive to accomplish electron transfer for systems where the $\text{A}^-|\text{A}$ system has a redox potential of about -0.6 V . The best yield calculated for a total pressure of 1 atm is obtained for the conditions of Fig. 5, curve 2a, except that, when $[\text{A}] = 0.1$, then $\Phi_{\text{H}_2} = 7\%$. This corresponds to a conversion of 14% of the photons absorbed. If a sensitizer can be found where little or no cage combination occurs (maximum electron transfer yield of unity) then a Φ_{H_2} of 20% can be achieved under the same conditions, thus converting 40% of the absorbed photons to hydrogen. Despite the low yields obtained in the present modelling the above numbers justify the search for more appropriate sensitizers and acceptors and for highly active and selective catalysts.

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Appendix A

The following expressions are used for the redox potentials in volts [A1]:

$$\text{H}_2|\text{H}^+ \quad E_1 = -0.0591\text{pH} - \frac{0.0591}{2} \log(p_{\text{H}_2}(\text{atm})) \quad (\text{A1})$$

$$\text{H}_2\text{O}|\text{O}_2 \quad E_2 = 1.230 - 0.0591\text{pH} + \frac{0.0591}{4} \log(p_{\text{O}_2}(\text{atm})) \quad (\text{A2})$$

$$\text{Ru}(\text{bpy})_3^{2+}|\text{Ru}(\text{bpy})_3^{3+} \quad E_3 = 1.260 + 0.0591 \log \left(\frac{[\text{Ru}(\text{bpy})_3^{3+}]}{[\text{Ru}(\text{bpy})_3^{2+}]} \right) \quad (\text{A3})$$

When A is MV the redox potential is

$$\text{MV}^+|\text{MV}^{2+} \quad E_4 = -0.445 + 0.0591 \log \left(\frac{[\text{MV}^{2+}]}{[\text{MV}^+]} \right) \quad (\text{A4})$$

We assume that Henry's law is applicable to hydrogen and oxygen and use the following relationships:

$$p_{\text{O}_2}(\text{atm}) = 827[\text{O}_2] \quad (\text{A5})$$

$$p_{\text{H}_2}(\text{atm}) = 1.4 \times 10^3[\text{H}_2] \quad (\text{A6})$$

where the concentrations are expressed in moles per litre.

The above equation gives the equilibrium constants K_{10} and K_{11} as

$$K_{10} = \frac{[\text{H}^+][\text{O}_2]^{1/4}[\text{Ru}(\text{bpy})_3^{2+}]}{[\text{Ru}(\text{bpy})_3^{3+}]} = 0.60 \quad (\text{A7})$$

$$K_{11} = \frac{[\text{MV}^{2+}][\text{H}_2]^{1/2}[\text{OH}^-]}{[\text{MV}^+]} = 9.05 \times 10^{-9} \quad (\text{A8})$$

using $[\text{H}^+][\text{OH}^-] = 10^{-14}$.

The importance of taking into account the equilibria is easily seen. With a catalyst and $p_{\text{H}_2} = 1$ atm at pH 7.5, $[\text{MV}^{2+}]/[\text{MV}^+] = 1$.

Reference for Appendix A

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