METALLOPORPHYRIN-PHOTOSENSITIZED FORMATION OF HYDROGEN FROM ORGANIC AND INORGANIC SUBSTRATES*

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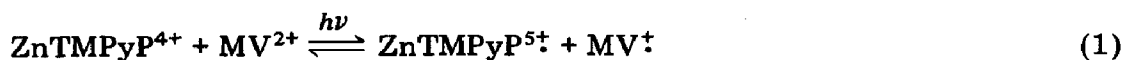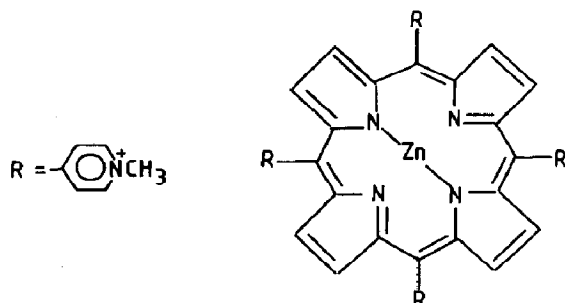*Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London W1X 4BS (Gt. Britain)*

Summary

In outgassed aqueous solution porphyrins can be photoreduced to give a π radical anion, a phlorin or a chlorin. The type of product formed depends on the nature of the porphyrin, the central metal ion and the solution pH. Porphyrins have been identified that form stable π radical anions and phlorins. These species, unlike the chlorins, are oxidized back to the original porphyrin by air and, depending on the pH, they can reduce water to hydrogen in the presence of a platinum catalyst. Thus irradiation of these porphyrins in aqueous solution containing an electron donor and colloidal platinum leads to hydrogen formation. Various electron donors have been used, including H_2S, hydrogenated nicotinamide adenine dinucleotide (NADH), formic acid, hydroxylamine and ethanol. The efficiency of hydrogen production depends markedly on the type of donor used and NADH is particularly effective. Possible ways of using NADH/NAD^+ as a reversible redox couple are considered.
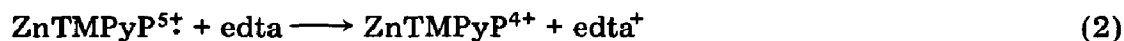
1. Introduction

Nature makes extensive use of metalloporphyrins as solar energy collectors and electron-transferring agents, and synthetic porphyrins have found prominent use as photosensitizers for both hydrogen [1] and oxygen [2, 3] formation from water. These compounds absorb intensely in the visible region of the spectrum and the triplet excited state lifetimes are often very long in outgassed solution [4]. For closed-shell metalloporphyrins electrons can be added to or removed from the π system at convenient potentials and, in many cases, the electrochemistry is fully reversible [5]. Such findings, together with their stability, variety and ease of synthesis, suggest that metalloporphyrins could be ideal photosensitizers for the collection and storage of solar energy.

Previously, it has been found that zinc(II) *meso*-tetrakis(*N*-methyl-4-pyridyl)porphine (ZnTMPyP^{4+}) is a particularly good sensitizer for the reduction of methylviologen (MV^{2+}) in acidic aqueous solution [6, 7]:

$$R = -\langle O \rangle \overset{+}{N}CH_3$$

$$ZnTMPyP^{4+} + MV^{2+} \underset{hv}{\rightleftharpoons} ZnTMPyP^{5\dot{+}} + MV^{\dot{+}} \tag{1}$$

At low ionic strength the quantum efficiency for formation of redox ion products is about 80% [8] but the high rate constant for reverse electron transfer reduces the photostationary state concentration of products to a very low level. In the presence of ethylenediaminetetraacetic acid (edta) reverse electron transfer is inhibited and reduced viologen accumulates in solution:

$$ZnTMPyP^{5\dot{+}} + edta \longrightarrow ZnTMPyP^{4+} + edta^{+} \tag{2}$$

$$edta^{+} \longrightarrow products \tag{3}$$

Since colloidal platinum catalyses the reduction of protons by MV^{+} with high efficiency (at pH 5)

$$2\,MV^{\dot{+}} + 2H^{+} \underset{Pt}{\rightleftharpoons} 2MV^{2+} + H_2 \tag{4}$$

the system represents one of the most effective chemical means for the photoproduction of hydrogen using visible light. Under optimized conditions the quantum efficiency for formation of hydrogen is 60% [7] but the stability of the reagents (ZnTMPyP^{4+} and MV^{2+}) is not high and the longevity of the system is poor.

Some improvement in the stability can be obtained by omitting the viologen relay. This latter system can be described as a "reductive cycle"

$$
\begin{array}{c}
H^{+} \\
Pt \\
\frac{1}{2}H_2
\end{array}
\left)
\begin{array}{c}
ZnTMPyP^{3\dot{+}} \\
hv \\
ZnTMPyP^{4+}
\end{array}
\right)
\left(
\begin{array}{c}
edta^{+} \\
products \\
edta
\end{array}
\right.
\tag{5}
$$

in which the π radical anion of the porphyrin is used to reduce water to hydrogen [9]. The quantum efficiency for hydrogen formation is only about

7% but in the presence of high concentrations of platinum the longevity can be quite good. However, hydrogen is produced from the system at the expense of destroying the donor (edta, ascorbate, triethylamine, triethanolamine etc.) and therefore the system has no real practical importance. Also, although the stability of the metalloporphyrin is relatively high it is still well below that required for a practical solar energy storage device.

In this paper we consider possible cycles for hydrogen production from organic and inorganic substrates using metalloporphyrins as electron relays and photosensitizers. The aims of the work are to identify systems of increased stability and versatility and to use alternative electron donors. The donors considered here include ethanol, glucose, lactate, H_2S, hydrogenated nicotinamide adenine dinucleotide (NADH), carboxylic acids and hydroxylamine, many of which are readily available from biological sources or as waste industrial materials. Ultimately, the electron donor will have to be water and some consideration is given to this point.

2. Reduction of metalloporphyrins

Let us consider only cycles in which the excited state metalloporphyrin is reduced by an electron donor and the reduced form of the porphyrin is used to generate hydrogen from water. For simplicity, we shall use only $TMPyP^{4+}$ complexes (hereafter abbreviated to P) although the nature of the water-solubilizing group is known to have a pronounced influence on the chemistry of reduced porphyrins [10]. In most cases, however, it is the $TMPyP^{4+}$ complexes that exhibit the highest levels of stability following reduction.

Two distinct pathways need to be considered for the reduction of a metalloporphyrin, *i.e.* metal-centred reductions and ring-centred reductions. The former case occurs for transition metal porphyrins, such as $Mn^{III}P$, $Fe^{III}P$ and $Rh^{III}P$, and results in the formation of the corresponding lower valent metalloporphyrin. However, because the excited state lifetimes of most transition metal porphyrins are short (owing to paramagnetic or charge transfer effects), the efficiency of the photochemistry is usually low. For example, irradiation of $Mn^{III}P$ in water [11] or aqueous edta results in the formation of $Mn^{II}P$ with quantum yields of 10^{-5} and 10^{-3} respectively:

$$Mn^{III}P + edta \xrightarrow{h\nu} Mn^{II}P + edta^+ \qquad (6)$$

with a feedback arrow from the product back to $Mn^{III}P$ labelled O_2.

The original metalloporphyrin is readily obtained by aeration of the solution, but the redox potential for the Mn^{II}/Mn^{III} couple is such that hydrogen formation cannot be observed even in the presence of a platinum catalyst. Similar photochemistry is observed with $Fe^{III}P$ and $Rh^{III}P$, and the latter system is of some interest since the triplet lifetime is fairly long (120 μs) and

$Rh^{II}P$ is able to form a hydride in neutral solution [12]. However, as with $Fe^{II}P$ and $Mn^{II}P$, no hydrogen is formed upon irradiation in the presence of edta and a platinum catalyst. Consequently, the metal-centred reductions seem to have no application for hydrogen formation.

Porphyrins and many diamagnetic metalloporphyrins can be reduced by addition of an electron to the π system to form a π radical anion. This is a general reaction for a wide range of porphyrins (*e.g.* $2H^+$, Zn^{2+}, Al^{3+}, Sn^{4+} and P^{5+}) and the π radical anions have been characterized by absorption spectroscopy using pulse radiolytic reduction [10, 13]. Figure 1 shows the absorption spectrum of the π radical anion as formed by irradiation of $Sn^{IV}P$ in aqueous solution (pH 13) containing 0.01 M edta.

$$Sn^{IV}P + edta \xrightarrow{h\nu} Sn^{IV}P^{\bar{\cdot}} + edta^+ \tag{7}$$

$$Sn^{IV}P + edta^+ \longrightarrow Sn^{IV}P^{\bar{\cdot}} + edta^{2+} \tag{8}$$

The radical has intense absorption bands at 445 and 695 nm and the spectrum agrees well with that found by pulse radiolytic reduction [10, 13]. For most metalloporphyrins the π radical anions were found to be unstable with respect to disproportionation and, at pH >12, only the radicals derived from $Sn^{IV}P$, $In^{III}P$ and P^VP were stable on storage in the absence of air. Even here the radicals became unstable when the solution was neutralized.

Disproportionation of the π radical anions leads to formation of the dianion which normally exists in aqueous solution in the monoprotonated form (termed the phlorin). Thus, irradiation of $Sn^{IV}P$ in water (pH 7) containing 0.01 M edta gives rise to the characteristic absorption spectrum of the phlorin (Fig. 1):
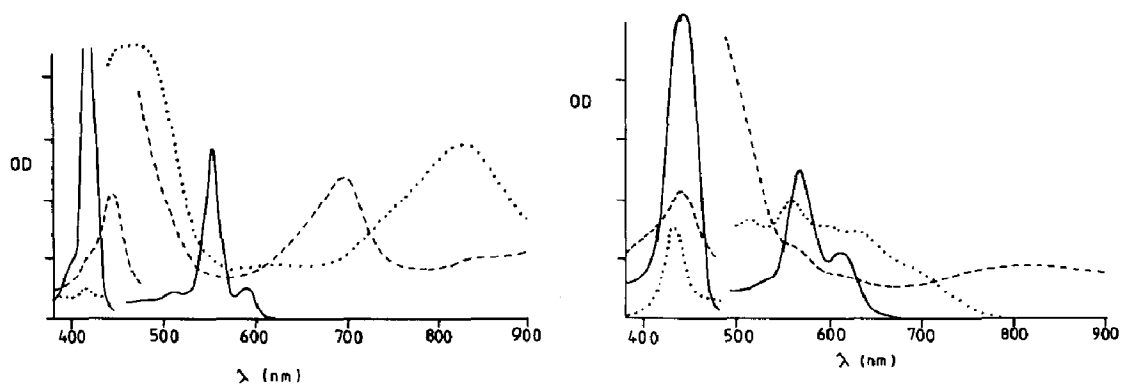
$$2Sn^{IV}P^{\bar{\cdot}} + H^+ \rightleftharpoons Sn^{IV}P + Sn^{IV}PH^- \tag{9}$$

Fig. 1. Absorption spectra of the products formed on irradiation of $Sn^{IV}P$ in aqueous solution containing 0.01 M edta: ———, $Sn^{IV}P$; — — —, the π radical anion formed at pH 13; ·······, the phlorin formed at pH 7. (Magnification, 7×.)

Fig. 2. Absorption spectra of the products formed on irradiation of ZnP in aqueous solution containing 0.01 M edta: ———, ZnP; — — —, the phlorin formed at pH 13; ·······, hydroporphyrins formed at pH 7. (Magnification, 6×.)

For most porphyrins, the phlorin is stable in outgassed aqueous solution, but only for H_2P, $Sn^{IV}P$ and P^VP are the phlorins stable over a wide pH range. In the other cases, the presence of protons causes rearrangement of the phlorin to the chlorin. This effect is shown in Fig. 2 for ZnP where the phlorin is formed at pH 13 but the chlorin is the sole product at pH <10. Table 1 gives a summary of the products found in typical irradiations in the presence of edta.

In general the π radical anions and phlorins can be regarded as reversible couples but the chlorins are irreversible. On aeration, the radicals and phlorins are oxidized back to the original porphyrin with little, if any, loss of the chromophore. Chlorins are stable towards aerial oxidation. Furthermore, given favourable thermodynamics both the radical and the phlorin are able to reduce water to hydrogen in the presence of colloidal platinum but, again, the chlorin will not give rise to hydrogen formation:

$$2Sn^{IV}P^{\cdot-} + 2H^+ \overset{Pt}{\rightleftharpoons} 2Sn^{IV}P + H_2 \tag{10}$$

$$Sn^{IV}PH^- + H^+ \overset{Pt}{\rightleftharpoons} Sn^{IV}P + H_2 \tag{11}$$

Consequently, the formation of stable π radical anions or phlorins represents a good means of reducing water to hydrogen whereas formation of the chlorin leads to a loss in the hydrogen evolving capacity of the system. We can now consider some possible cycles for hydrogen formation based on the conclusions given in Table 1.

TABLE 1

Products formed on visible light irradiation of metalloporphyrins in an outgassed aqueous solution containing 0.01 M ethylenediaminetetraacetic acid

MP	pH	Product
H_2P	0 - 14	Phlorin
AlP, ZnP	12 - 14	Phlorin
	<12	Chlorin
MgP, CdP	12 - 14	Phlorin
	8 - 12	Chlorin
	<8	Demetallation
InP	12 - 14	Anion
	9 - 12	Phlorin
	<9	Chlorin
SnP, PP	11 - 14	Anion
	<11	Phlorin

MP, metalloporphyrin.

3. Cleavage of H_2S

H_2S is readily available as a waste product from several important chemical processes and is a well-known poison. Several groups [14 - 16] have recently reported photochemical systems for the cleavage of H_2S based on metal-oxide-coated semiconductor powders and, in particular, CdS/RuO_2 seems to be a very efficient photocatalyst. Also, Okura *et al.* [17] have reported the use of H_2S as an electron donor for hydrogen-evolving photo-systems based on a metalloporphyrin sensitizer.

We attempted to photodissociate H_2S using a porphyrin/phlorin cycle. The first system used employed CdP as the photosensitizer but it was found that the presence of sulphide ions caused demetallation of the porphyrin, even at pH 13:

$$CdP + H_2S \longrightarrow CdS + H_2P \tag{12}$$

Somewhat better results were obtained with ZnP. Thus, irradiation of ZnP in water (pH 13) containing 0.1 M Na_2S resulted in the formation of the phlorin which was stable in the absence of air:

$$ZnP + HS^- \xrightarrow{h\nu} ZnPH^- + S \tag{13}$$

When colloidal platinum was added to the solution, small amounts of hydrogen were generated:

$$ZnPH^- + H^+ \underset{}{\overset{Pt}{\rightleftharpoons}} ZnP + H_2 \tag{14}$$

However, conversion of phlorin into porphyrin was not quantitative and it soon became clear that the high concentrations of sulphide ions present in solution poisoned the platinum catalyst. Studies with other catalysts showed that RuO_2 and WC gave better performances than platinum but, even so, the yield of hydrogen remained low. Compared with a CdS/RuO_2 photosystem, which gave a rate of hydrogen formation of 120 cm^3 H_2 (1 solution)$^{-1}$ h^{-1}, the ZnP/WC system gave very little hydrogen. Typical rates for the latter system were around 2 cm^3 H_2 (1 solution)$^{-1}$ h^{-1}. Lowering the pH and varying the concentrations of reactants gave no marked improvements.

4. Dissociation of hydroxylamine

We became interested in the possible photodissociation of hydroxylamine, not because it is a readily available electron donor but because it might be a model compound for the cleavage of urea into ammonia and CO_2. So far we have not been able to achieve the latter reaction but the dissociation of hydroxylamine is possible when $Sn^{IV}P$ is used as the photosensitizer. Thus, irradiation of $Sn^{IV}P$ in a 1 M HCl solution containing 0.2 M hydroxylamine results in very inefficient formation of the phlorin. Under these conditions the phlorin is protonated:

$$Sn^{IV}P + 2NH_3OH^+ \xrightarrow{h\nu} Sn^{IV}PH_2 + N_2 + 2H_3O^+ \tag{15}$$
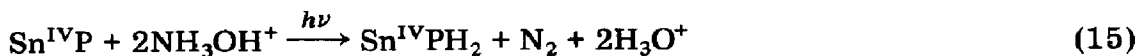
As before, the phlorin can be converted back to the original porphyrin on aeration or on addition of colloidal platinum:

$$Sn^{IV}PH_2 \underset{}{\overset{Pt}{\rightleftharpoons}} Sn^{IV}P + H_2 \tag{16}$$

The overall efficiency for hydrogen generation from this system is extremely low, despite the favourable energetics, and typical hydrogen yields were only about 1 - 2 μl (l solution)$^{-1}$. Thus, the system offers no real interest.

5. Dissociation of carboxylic acids

Of the carboxylic acids, the easiest to dissociate is formic acid:

$$HCOOH \longrightarrow H_2 + CO_2 \qquad \Delta G^\circ = -38.5 \text{ kJ mol}^{-1} \tag{17}$$
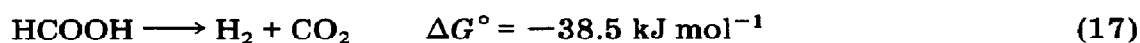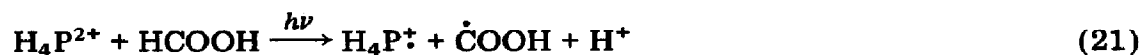
This process is thermodynamically downhill and can be achieved by stirring a concentrated solution of formic acid with Pd–C at about 60 °C [18]. The fact that the photodissociation of formic acid can be realized at room temperature offers a small energy saving but the system will only become important when large quantities of formic acid are readily available. At the moment, formic acid can be obtained from certain plants, by alkaline hydrolysis of glucose and from the photoreduction of CO_2 [19]. Unfortunately, the efficiency for the latter process is extremely low at the present time but it is a process that merits detailed study. If it should ever become efficient then formic acid has great potential as a hydrogen carrier:

$$2CO_2 + 2H_2O \xrightarrow{h\nu} 2HCOOH + O_2 \tag{18}$$

$$HCOOH \xrightarrow{h\nu} H_2 + CO_2 \tag{19}$$

It was found that formic acid could reduce the excited states of several porphyrins. The most efficient photochemistry was observed for the porphyrin diacid as formed by the addition of two extra protons to the porphyrin:

$$H_2P + 2H^+ \rightleftharpoons H_4P^{2+} \tag{20}$$

Thus, irradiation of the diacid in 1 M $HClO_4$ solution containing 0.5 M formic acid resulted in formation of the phlorin (Fig. 3). Flash photolysis showed the intermediate formation of a π radical anion which decayed by mixed kinetics. CO_2 was also formed during the reaction so that the overall process can be written in the form
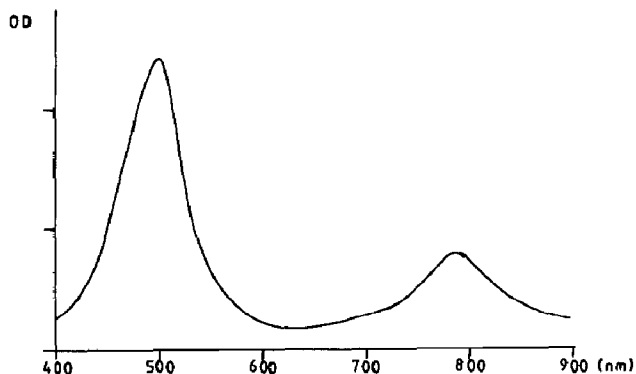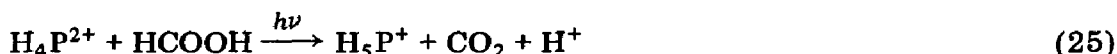
$$H_4P^{2+} + HCOOH \xrightarrow{h\nu} H_4P^{\cdot+} + \dot{C}OOH + H^+ \tag{21}$$

$$H_4P^{2+} + \dot{C}OOH \longrightarrow H_4P^{\cdot+} + CO_2 + H^+ \tag{22}$$
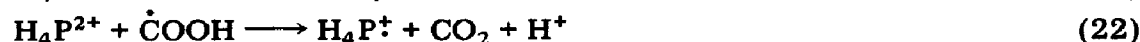
Fig. 3. Absorption spectrum of the phlorin formed on irradiation of H_4P^{2+} in 1 M $HClO_4$ containing 0.5 M formic acid.

$$H_4P^{\dot{+}} + \dot{C}OOH \longrightarrow H_5P^+ + CO_2 \qquad (23)$$

$$H^+ + 2H_4P^{\dot{+}} \rightleftharpoons H_4P^{2+} + H_5P^+ \qquad (24)$$

Hence the overall reaction becomes

$$H_4P^{2+} + HCOOH \xrightarrow{h\nu} H_5P^+ + CO_2 + H^+ \qquad (25)$$

and the resultant phlorin is extremely stable in the absence of air.

On addition of colloidal platinum to the solution, no hydrogen was formed. This is due to the poor thermodynamics since the redox potential for this particular porphyrin/phlorin couple is close to 0 V [20]. Replacing the porphyrin with more reducing porphyrin diacids resulted in identical photochemistry but now the phlorin can reduce water to hydrogen. This effect is shown in Fig. 4 where it is seen that the diacid derived from *meso*-tetrakis(4-sulphonatophenyl)porphyrin (H_4TSPP^{2-}) is an effective photosensitizer for hydrogen production. In this system irradiation of the solution with light of wavelength greater than 620 nm gave rise to formation of about
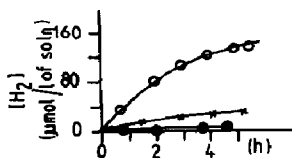

Fig. 4. Yields of hydrogen formed on irradiation of the diacids in 1 M $HClO_4$ containing 0.5 M formic acid: ○, H_4TSPP^{2-}; ×, H_4TAPP^{6+}; ●, H_4TMPyP^{6+}. (H_4TAPP^{6+} is the conjugate diacid formed from *meso*-tetrakis(N,N,N-trimethyl-4-anilinium)porphine.)
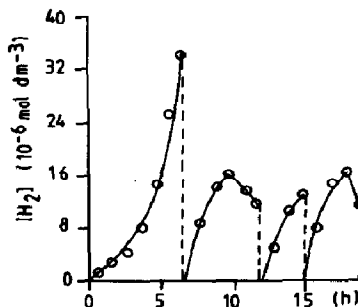
Fig. 5. Effect of flushing the solution with nitrogen for the H_4TSPP^{2-}-photosensitized dissociation of formic acid.

0.16 cm^3 H$_2$ (l solution)$^{-1}$. Removing the evolved hydrogen by flushing with nitrogen restored the hydrogen-evolving capacity, as shown by Fig. 5. By repeated flushing with nitrogen it was possible to convert a reasonable percentage (15%) of the formic acid into hydrogen and CO$_2$ at 15 °C (no hydrogen is formed in the absence of light at this temperature). This reaction, which took several days to accomplish, corresponds to a turnover number with respect to H$_4$TSPP^{2-} of about 5000 and even then the chromophore had not been destroyed. Thus the diacid shows remarkable stability under such conditions. These findings suggest that the limiting yields of hydrogen, as shown by Fig. 4, are set by thermodynamic barriers:

$$H_5P^+ + H^+ \underset{}{\overset{Pt}{\rightleftharpoons}} H_4P^{2+} + H_2 \qquad (26)$$
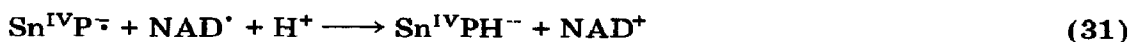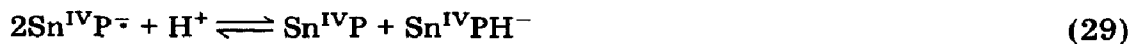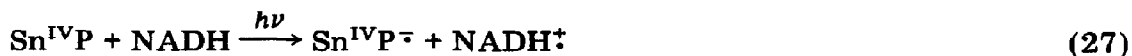
Therefore it is possible that the overall efficiency of the process can be improved by locating even more powerfully reducing metalloporphyrins that form acid-stable phlorins.

In similar studies it was found that other carboxylic acids (*e.g.* acetic and propionic acids) could be decomposed with H$_4$TSPP^{2-}. The overall reaction mechanisms were similar to that given above whilst the total yields of hydrogen were slightly lower than those found with formic acid.

6. Oxidation of hydrogenated nicotinamide adenine dinucleotide

The biologically important reductant NADH can be used to reduce the triplet excited state of most metalloporphyrins over a fairly wide pH range. The reactions are normally efficient and, in accordance with Table 1, the products can be chlorins, phlorins or π radical anions. Thus irradiation of Sn^{IV}P in aqueous solution at pH 13 containing 10^{-3} M NADH results in the formation of the stable π radical anion. When the reaction is performed at pH 7.5, the observed product is the phlorin:

$$Sn^{IV}P + NADH \overset{h\nu}{\longrightarrow} Sn^{IV}P^{\overline{\cdot}} + NADH^{\dot{+}} \qquad (27)$$

$$NADH^{\dot{+}} \underset{pK\,=\,-4}{\rightleftharpoons} NAD^{\cdot} + H^+ \qquad (28)$$

$$2Sn^{IV}P^{\overline{\cdot}} + H^+ \rightleftharpoons Sn^{IV}P + Sn^{IV}PH^- \qquad (29)$$

$$Sn^{IV}P + NAD^{\cdot} \longrightarrow Sn^{IV}P^{\overline{\cdot}} + NAD^+ \qquad (30)$$

$$Sn^{IV}P^{\overline{\cdot}} + NAD^{\cdot} + H^+ \longrightarrow Sn^{IV}PH^- + NAD^+ \qquad (31)$$

The overall process requires one photon to drive a two-electron reduction of the porphyrin:

$$Sn^{IV}P + NADH \overset{h\nu}{\longrightarrow} Sn^{IV}PH^- + NAD^+ + H^+ \qquad (32)$$
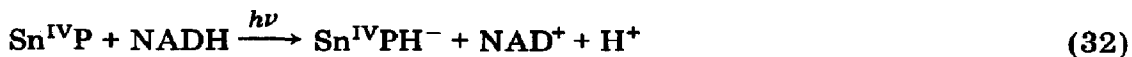
For light with λ = 550 nm, the quantum yield for formation of the phlorin (pH 7.5) was 0.6 (for an NADH concentration of 2 × 10^{-3} M). It should be

noted that this cycle is extremely clean and that there is no chlorin formation under such conditions.

When colloidal platinum is present, irradiation results in the formation of hydrogen and the phlorin is no longer observed as a reaction product. Depending on pH, the phlorin, the π radical anion and NAD$^\bullet$ are all capable of reducing protons on the surface of a platinum catalyst. The quantum yield for formation of hydrogen was found to be 0.43 at pH 7.5. Although very efficient and stable, the above cycle is still sacrificial in that the hydrogen is evolved at the expense of oxidation of NADH to NAD$^+$ and there is an increase in pH:
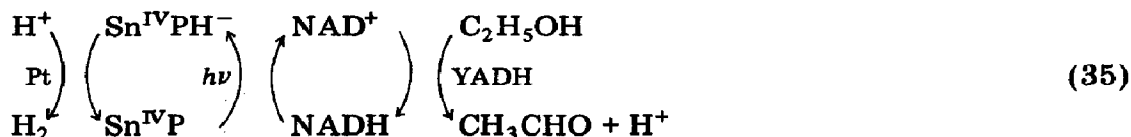
$$H_2O + NADH \xrightarrow{h\nu} NAD^+ + H_2 + OH^- \tag{33}$$

7. Regeneration of hydrogenated nicotinamide adenine dinucleotide

Regeneration of NADH from NAD$^+$ can be achieved readily using ethanol and an enzyme catalyst such as yeast alcohol dehydrogenase (YADH):

$$C_2H_5OH + NAD^+ \xrightarrow{\text{YADH}} CH_3CHO + NADH + H^+ \tag{34}$$

Thus irradiation of Sn^{IV}P with green light in nitrogen-purged aqueous solution at pH 7.5 containing NADH, colloidal platinum, YADH and ethanol (2 vol.%) results in sustained generation of hydrogen [21]. In a typical experiment the rate of hydrogen formation was about 440 cm^3 (1 solution)$^{-1}$ h^{-1}. On prolonged irradiation turnover numbers for NADH and YADH of 86 and 131 000 respectively were obtained, although that given for NADH is not exhaustive. Only a small fraction of the metalloporphyrin is lost (via chlorin formation) whilst the ethanol is converted quantitatively into acetaldehyde and hydrogen and the quantum yield for hydrogen formation remains at 0.43. The solution pH remains constant during the overall reaction [21] and the rate of hydrogen formation shows no significant decrease until the YADH or ethanol has been consumed.

Overall, the photoreaction can be summarized by the following scheme:

$$\begin{array}{c} H^+ \\ Pt \\ H_2 \end{array} \Bigg) \begin{array}{c} Sn^{IV}PH^- \\ h\nu \\ Sn^{IV}P \end{array} \Bigg) \begin{array}{c} NAD^+ \\ \\ NADH \end{array} \Bigg) \begin{array}{c} C_2H_5OH \\ YADH \\ CH_3CHO + H^+ \end{array} \tag{35}$$

The dehydrogenation of ethanol

$$C_2H_5OH(l) \longrightarrow CH_3CHO(l) + H_2(g) \tag{36}$$

is thermodynamically uphill so that energy is stored during the reaction. The overall efficiency for storage of light energy is 9.4%. The idea of using an enzyme to regenerate the electron donor is not restricted to ethanol;

D-glucose or lactate could be used instead. Both give rise to efficient hydrogen production.

8. Water oxidation

Ultimately the electron donor must be water and some consideration should be given to this point. As a beginning, we can consider the NADH/NAD$^+$ couple as a reversible electron relay and try to reduce NAD$^+$ directly:

$$2NAD^+ + 2H_2O \longrightarrow 2NADH + O_2 + 2H^+ \tag{37}$$

Attempts to do this by reaction with the triplet excited states of several metalloporphyrins have not been successful. This is because the reaction is reversible and the NAD$^{\cdot}$ product undergoes dimerization rather than disproportionation:

$$\tag{38}$$

$$2NAD^{\cdot} \longrightarrow (NAD)_2 \tag{39}$$

Again, enzymes could play an important role in this reaction, as shown by the following scheme:

$$NAD^+ + 2MV^{\cdot +} + H^+ \overset{\textbf{enzyme}}{\rightleftharpoons} NADH + 2MV^{2+} \tag{40}$$

$$\tag{41}$$
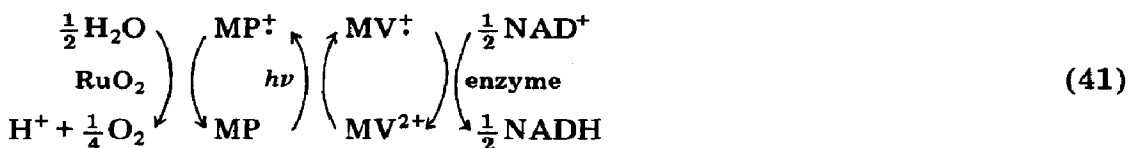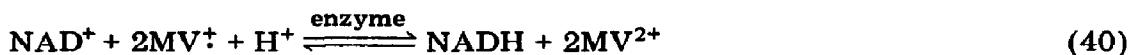
The essential feature of this scheme concerns the rate at which the enzyme can accept electrons from MV$^{\cdot +}$. In our experiments this rate occurs in the region of $0.1 - 1$ s^{-1} but it could be increased significantly by optimizing the concentrations of the enzyme and MV^{2+}. So far, the above scheme has not been realized but experiments are still at a very preliminary stage.

Acknowledgments

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