Photochemical Hydrogen Production from Ascorbic Acid Catalysed by Tris(2,2′-bipyridyl)ruthenium(II) and Hydridotris(triethylphosphine)-palladium(II)

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Hydrogen is produced catalytically, over a limited period of time, on photolysis of aqueous solutions containing $[PdH(PEt_3)_3]^+$, $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridyl), and ascorbic acid. Kinetic studies suggest a rate-determining electron transfer from photochemically produced $[Ru(bipy)_3]^+$ to $[PdH(PEt_3)_3]^+$ to give a palladium(I) radical from which hydrogen is rapidly produced. Termination of the hydrogen-producing reaction is shown to occur because $[PdH(PEt_3)_3]^{\cdot}$ is oxidised by product dehydroascorbic acid in a competing reaction to H_2 production, and because of substantial bleaching of the $[Ru(bipy)_3]^{2+}$.

The ability of $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridyl) to act as a photosensitiser [1] and, in particular, the fact that its photochemically excited state, $[Ru(bipy)_3]^{2+*}$, is able to act as either an electron donor [2] or an electron acceptor [3] have led to recent interest in its possible role in the photochemical production of hydrogen from water.

Most research in this area has concentrated [4,5] on the oxidative quenching of $[Ru(bipy)_3]^{2+*}$ by electron relays such as methyl viologen (1,1′-dimethyl-4,4′-bipyridinium dichloride),[4] $[Rh(bipy)_3]^{3+}$,[6,7] or TiO_2[8] to produce $[Ru(bipy)_3]^{3+}$ and the reduced form of the relay, which then reduces protons in the presence of a suitable redox catalyst (*e.g.* colloidal Pt [4,5]), while the $[Ru(bipy)_3]^{3+}$ is either reduced by an irreversible electron donor [4,5] or used to oxidise OH^- to O_2.[9] The rate of the oxygen-producing reaction is, however, only capable of competing with that of back electron transfer between reduced relay and oxidised sensitiser if catalysed by RuO_2.[10]

Work by Sutin and co-workers [11–14] has shown that hydrogen can also be produced photochemically from water and $[Ru(bipy)_3]^{2+}$ by a reductive cycle. Thus, ascorbic acid (H_2A),[11,13,14] Eu^{2+},[12] and SO_3^{2-} [11] all reductively quench $[Ru(bipy)_3]^{2+*}$ to give the strongly reducing $[Ru(bipy)_3]^+$. This, in the presence of certain Co^{II} complexes, reduces [12–14] protons to hydrogen apparently *via* unstable Co^I hydride intermediates. Quantum yields as high as 0.13 have been reported [14] using ascorbate as electron donor and $[Co(dmbipy)_n]^{2+}$ (dmbipy = 4,4′-dimethyl-2,2′-bipyridyl) as electron relay. The complex nature of the role of ascorbate ion has also been discussed.[15]

The main advantages of reductive systems of this kind are that they are totally homogeneous and hence light is not scattered or absorbed by colloidal particles and the roles of electron relay and redox catalyst are combined in one molecule. However, the production of $[Ru(bipy)_3]^+$ and O_2 in a photochemical reaction has not yet been demonstrated so that a sacrificial electron donor is always required.

We have recently shown [16] that $[MH(PEt_3)_3]^+$ (M = Pt or Pd) can be reduced with amalgam reducing agents to hydrogen and, at least for platinum, $[M(PEt_3)_3]$. Since the zero-valent products are readily protonated back to $[MH(PEt_3)_3]^+$ by water, these compounds should, in principle, be able to be used as electron relays for the production of hydrogen from water. However, attempts to catalyse the decomposition of water by irradiating solutions of $[Ru(bipy)_3]^{2+}$, $[MH(PEt_3)_3]^+$, and the disodium salt of ethylenediaminetetra-acetic acid (H_4edta) in water were unsuccessful.[16] The production of hydrogen on u.v. photolysis of solutions of $[MH(PEt_3)_3]^+$ is not believed [17–19] to involve intermolecular redox processes.

We have since carried out [20] electrochemical studies on these compounds and find that, although cyclic voltammograms measured at a mercury-drop electrode are highly complex, reduction of non-adsorbed $[MH(PEt_3)_3]^+$ does not occur at potentials less negative than *ca.* −1.0 (M = Pd) or *ca.* −1.5 V(M = Pt).† We also believe that reductions at these potentials are by two electrons to give $[MH(PEt_3)_3]^-$(ads).

Comparison of these redox potentials with that of $[Ru(bipy)_3]^{2+*}$ $[E^{\ominus}(3+/2+*) = -1.1\ V]$ [1] show that the excited state of the ruthenium complex is an insufficiently strong reducing agent to reduce $[MH(PEt_3)_3]^+$. However, $[Ru(bipy)_3]^+$ $[E^{\ominus}(2+/+) = -1.5\ V]$ [1] is a stronger reducing agent than $[Ru(bipy)_3]^{2+*}$ and it would appear that the monocation might reduce $[PdH(PEt_3)_3]^+$, although not $[PtH(PEt_3)_3]^+$. Accordingly, we have investigated the use of $[PdH(PEt_3)_3]^+$ as a combined relay and electron-transfer catalyst for the production of hydrogen from $[Ru(bipy)_3]^+$ and the results of these investigations are described below. A preliminary communication of some of these results has appeared.[19]

Results and Discussion

Solutions containing $[Ru(bipy)_3]^{2+}$, $[PdH(PEt_3)_3]^+$, and ascorbic acid in 0.4 mol dm^{-3} phosphate buffer (pH 2—7) produce hydrogen on photolysis with visible light (see Figure 1). Omission of any of the components listed above (except phosphate), or replacement of $[PdH(PEt_3)_3]^+$ by its platinum analogue,‡ causes negligible hydrogen production suggesting that all three of the components listed above are required in the hydrogen-producing sequence of reactions. Hydrogen production in these systems proceeds for *ca.* 24 h but then ceases. In a typical experiment, 5 cm^3 of a solution of pH 4.6 containing $[Ru(bipy)_3]^{2+}$ (6.5×10^{-7} mol), $[PdH(PEt_3)_3]^+$ (5.8×10^{-5} mol), and ascorbic acid (3.5×10^{-3} mol) produced a total of 1.2 cm^3 (4.9×10^{-5} mol) of H_2 at 25 °C. This corresponds to turnover numbers of *ca.* 150 for $[Ru(bipy)_3]^{2+}$ and 1.6 for $[PdH(PEt_3)_3]^+$, assuming that 1 mol of each produces 0.5 mol of H_2.§ Maximum quantum yields for

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† Voltages are relative to a saturated calomel electrode (s.c.e.).

‡ On some occasions hydrogen is produced on irradiation of solutions containing ascorbic acid, $[Ru(bipy)_3]^{2+}$, and $[PtH(PEt_3)_3]^+$, but we believe this only occurs when the solution contains colloidal platinum, which is known to catalyse the production of hydrogen from $[Ru(bipy)_3]^+$ and water.[21]

§ If the mechanism of Scheme 2 is followed, one mole of H_2 is produced per mole of $[PdH(PEt_3)_3]^+$ and the turnover number is 0.8.

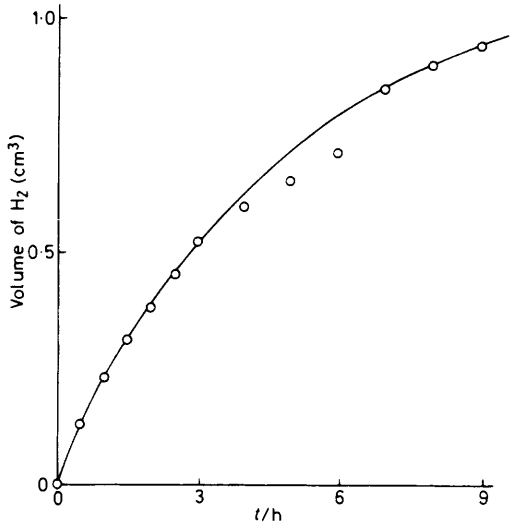

Figure 1. Plot of volume of hydrogen produced (298 K) against time from 5 cm^3 of solution: [Ru(bipy)$_3^{2+}$] = 1.74 × 10^{-4}, [PdH(PEt$_3$)$_3^+$] = 5.45 × 10^{-2}, H$_2$A = 0.7 mol dm^{-3}; at pH 4.6

Table. Quantum yield for hydrogen production at various pH [a]

pH	10$^3\Phi(H_2)$ [b]/mol einstein^{-1}
2.5	1.43
3.3	1.53
3.5	1.66
4.0	1.80
4.9	0.04
6.9	0.03

[a] [Ru(bipy)$_3^{2+}$] = 1.86 × 10^{-4}, [PdH(PEt$_3$)$_3^+$] = 5.6 × 10^{-2}, [H$_2$A] = 0.7 mol dm^{-3}. [b] Values corrected for fraction of [Ru(bipy)$_3$]$^{2+*}$ quenched by ascorbate ion. Maximum quantum yield for hydrogen production is 0.5.

hydrogen production are of the order of 2 × 10^{-3} (see Table). Phosphorus-31 n.m.r. studies on solutions before and after irradiation show that in both cases the major phosphorus-containing species is [PdH(PEt$_3$)$_3$]$^+$, although after photolysis singlet resonances at δ 65.6 and 40.8 p.p.m.† account for < 10% of the phosphorus in solution. These resonances can be attributed to PEt$_3$O and the hydroxy-bridged dimer [Pd$_2$(OH)$_2$(PEt$_3$)$_4$]$^{2+}$ which are formed, apparently *via* a hydroperoxy compound, [Pd(OOH)(PEt$_3$)$_3$]$^+$, on exposure of [PdH(PEt$_3$)$_3$]$^+$ to air.[22] Their origin in these photochemical reactions is uncertain, but they may arise from traces of oxygen in the nitrogen (see later) or from oxidation by dehydroascorbic acid formed during the photochemical production of hydrogen. Either way, their presence in such small quantities is unlikely to be responsible for the termination of the hydrogen-producing reaction. Indeed, solutions which have been partially air oxidised prior to irradiation still produce hydrogen on photolysis after degassing.

It is also possible that the resonance at δ 40.8 p.p.m. arises from [Pd(PEt$_3$)$_3$X]$^{n+}$ (X = OH$_2$, n = 2; X = O$_4$PH$_2$, n = 1) which is formed [19,22] on photolysis of solutions of [PdH(PEt$_3$)$_3$]$^+$ with u.v. light, but the yield of this product is very low when photolysis is carried out with visible light. We shall return to the subject of reaction termination below.

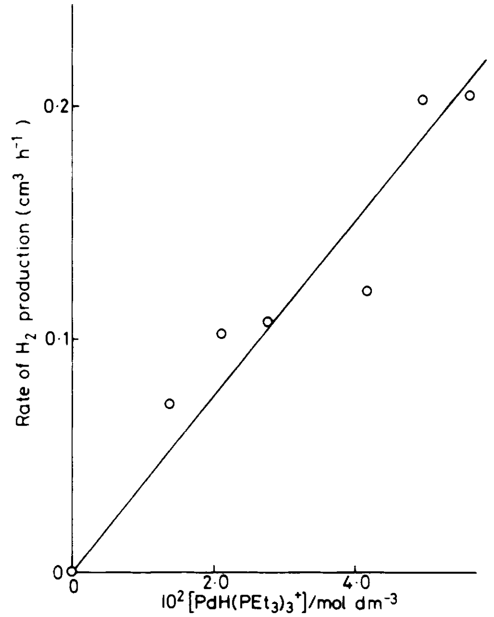

Figure 2. Plot of rate of hydrogen production against concentration of [PdH(PEt$_3$)$_3$]$^+$: 2 cm^3 of solution; [Ru(bipy)$_3^{2+}$] = 1.86 × 10^{-4}, [H$_2$A] = 0.7 mol dm^{-3}; at pH 6.88

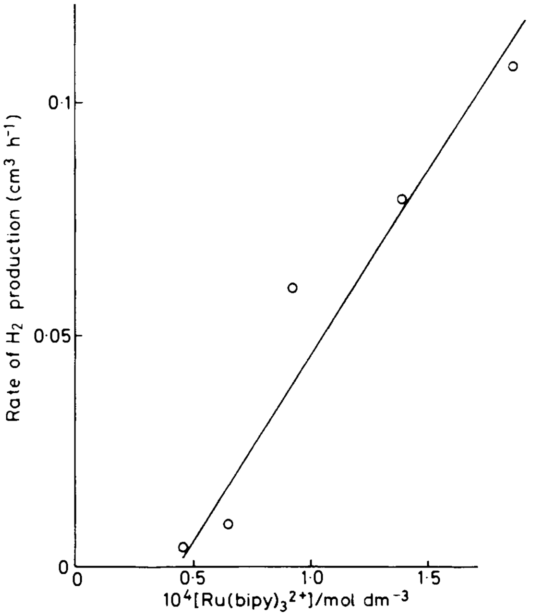

Figure 3. Plot of rate of hydrogen production against concentration of [Ru(bipy)$_3$]$^{2+}$: 2 cm^3 of solution; [PdH(PEt$_3$)$_3^+$] = 2.81 × 10^{-2}, [H$_2$A] = 0.7 mol dm^{-3}; at pH 6.88

Reaction Mechanism.—Although reproducibility of results has been a problem (see below), by following an identical procedure for each of the reactions (see Experimental section), it has been possible to show that the rate of hydrogen production is first order in [PdH(PEt$_3$)$_3^+$] (Figure 2) and in [Ru(bipy)$_3^{2+}$] (Figure 3), although the plot of rate against [Ru(bipy)$_3^{2+}$] does not pass through the origin.

The first-order dependence of the rate of hydrogen production on [Ru(bipy)$_3^{2+}$] and [PdH(PEt$_3$)$_3^+$], coupled with the observation that [Ru(bipy)$_3$]$^+$ is the major ruthenium-

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† Phosphorus chemical shifts are to low frequency of external 85% H$_3$PO$_4$.

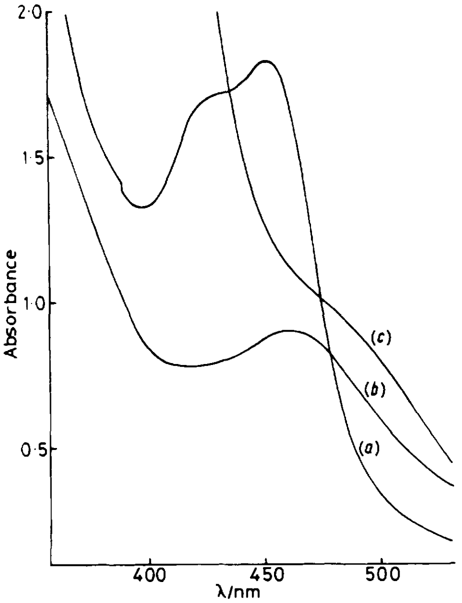


Figure 4. U.v.–visible spectra taken during photolysis of a solution containing ascorbic acid (0.7 mol dm^{-3}), $[\mathrm{Ru(bipy)_3}]^{2+}$ (5.1 × 10^{-5} mol dm^{-3}), and $[\mathrm{PdH(PEt_3)_3}]^{+}$ (2 × 10^{-2} mol dm^{-3}) in phosphate buffer (2 cm^3, pH 6.88): (*a*) initially, (*b*) after 2 h photolysis, (*c*) after 72 h photolysis ($\lambda_{max.}$ of shoulder *ca.* 490 nm). At higher concentrations of $[\mathrm{PdH(PEt_3)_3}]^{+}$ (8 × 10^{-2} mol dm^{-3}), the major ruthenium species during photolysis is $[\mathrm{Ru(bipy)_3}]^{2+}$. An identical spectrum to (*b*) is obtained on photolysis of $[\mathrm{Ru(bipy)_3}]^{2+}$ and ascorbic acid in phosphate buffer for 45 min

$$[\mathrm{Ru(bipy)_3}]^{2+} \xrightarrow{h\nu} [\mathrm{Ru(bipy)_3}]^{2+*}$$

$$[\mathrm{Ru(bipy)_3}]^{2+*} + \mathrm{HA^-} \longrightarrow [\mathrm{Ru(bipy)_3}]^{+} + \mathrm{A^{\bullet -}} + \mathrm{H^+}$$

$$\mathrm{H^+} + 2\mathrm{A^{\bullet -}} \longrightarrow \mathrm{A} + \mathrm{HA^-}$$

$$[\mathrm{Ru(bipy)_3}]^{+} + [\mathrm{PdH(PEt_3)_3}]^{+} \longrightarrow [\mathrm{PdH(PEt_3)_3}]^{\bullet} + [\mathrm{Ru(bipy)_3}]^{2+}$$

Scheme 1. Proposed mechanism for the photoproduction of $[\mathrm{PdH(PEt_3)_3}]^{\bullet}$ from aqueous solutions containing $[\mathrm{Ru(bipy)_3}]^{2+}$, $[\mathrm{PdH(PEt_3)_3}]^{+}$, and ascorbic acid ($\mathrm{H_2A}$ = ascorbic acid, $\mathrm{A^{\bullet -}}$ = ascorbate radical anion, A = dehydroascorbic acid)

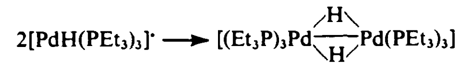
containing species present in solution during photolysis [Figure 4(*b*)] suggests that $[\mathrm{Ru(bipy)_3}]^{+}$ is formed rapidly by reduction of $[\mathrm{Ru(bipy)_3}]^{2+*}$ by ascorbic acid, as described by Sutin [11,13,14] (see Scheme 1). This is then followed by rate-determining † electron transfer from $[\mathrm{Ru(bipy)_3}]^{+}$ to $[\mathrm{PdH(PEt_3)_3}]^{+}$.

Although electrochemical experiments suggest that $[\mathrm{PdH(PEt_3)_3}]^{+}$(aq) undergoes a two-electron reduction at a mercury electrode, the catalytic production of hydrogen at such an electrode apparently involves [20] one-electron reduction of $[\mathrm{PdH(PEt_3)_3}]^{+}$ (ads). Both of these reductions occur at considerably more negative potentials than that of the couple $[\mathrm{Ru(bipy)_3}]^{3+/+}$ (*ca.* 0 V)[1] and hence we conclude that $[\mathrm{Ru(bipy)_3}]^{+}$ must act as a one-electron reductant of $[\mathrm{PdH(PEt_3)_3}]^{+}$ even though the palladium complex is not adsorbed. This process will lead to the neutral radical, $[\mathrm{PdH(PEt_3)_3}]^{\bullet}$, whose subsequent fate is a matter of conjecture, but it must almost certainly obtain another electron before or after protonation. This electron can be provided by another mole of $[\mathrm{Ru(bipy)_3}]^{+}$, in which case the remainder of the cycle will be as shown in Scheme 2 and analogous to that proposed [20] for the electrochemical behaviour of $[\mathrm{MH(PEt_3)_3}]^{+}$ (M = Pt or Pd).

$$[\mathrm{PdH(PEt_3)_3}]^{\bullet} + \mathrm{H^+} + [\mathrm{Ru(bipy)_3}]^{+} \longrightarrow [\mathrm{Pd(PEt_3)_3}] + [\mathrm{Ru(bipy)_3}]^{2+} + \mathrm{H_2}$$

$$[\mathrm{Pd(PEt_3)_3}] + \mathrm{H^+} + [\mathrm{Ru(bipy)_3}]^{+} \longrightarrow [\mathrm{PdH(PEt_3)_3}]^{+}$$

Scheme 2. Possible mechanism for production of hydrogen from $[\mathrm{PdH(PEt_3)_3}]^{\bullet}$ using $[\mathrm{Ru(bipy)_3}]^{+}$ as the source of a second electron



$$2[\mathrm{PdH(PEt_3)_3}]^{\bullet} \longrightarrow [\mathrm{(Et_3P)_3Pd(\mu\text{-}H)_2Pd(PEt_3)_3}]$$

$$[\{\mathrm{PdH(PEt_3)_3}\}_2] \longrightarrow 2[\mathrm{Pd(PEt_3)_3}] + \mathrm{H_2}$$

$$[\mathrm{Pd(PEt_3)_3}] + \mathrm{H^+} \longrightarrow [\mathrm{PdH(PEt_3)_3}]^{+}$$

Scheme 3. Alternative mechanism for production of hydrogen from $[\mathrm{PdH(PEt_3)_3}]^{\bullet}$ *via* a binuclear intermediate

Alternatively, it is possible that the second electron derives from another mole of $[\mathrm{PdH(PEt_3)_3}]^{\bullet}$ to give the hydrido-bridged dimer, shown in Scheme 3. A similar complex has been reported [23] to be formed on reaction of $[\mathrm{Pd(PEt_3)_3}]$ with hydrogen ‡ under pressure. Loss of hydrogen and protonation then complete the cycle.

The effect of varying the pH of the solution is shown in the Table. The quantum yield for hydrogen production increases gradually with increasing pH until pH *ca.* 4 and then drops dramatically at high pH, although hydrogen is still produced at pH 7.

A similar pH dependence has been observed [14] when $[\mathrm{Co(bipy)_3}]^{2+}$ is used as an electron relay for the production of hydrogen from $[\mathrm{Ru(bipy)_3}]^{+}$ and water. Although a number of different reactions occur in this system, it has been suggested that at high pH the Co$^{\mathrm{I}}$ intermediate and its hydride (obtained by protonation) are rapidly oxidised by ascorbate radical anion whereas at low pH the rate of production of hydrogen drops because of oxidation of these complexes by the protonated bipyridyl in solution.[14]

In our system it is probable that inhibition at high pH also occurs because of oxidation of $[\mathrm{PdH(PEt_3)_3}]^{\bullet}$ by ascorbate radical anion but the rather less precipitous decline in hydrogen production as the pH is lowered clearly cannot arise from oxidation of $[\mathrm{PdH(PEt_3)_3}]^{\bullet}$ by protonated bipyridyl since there is no free bipyridyl in solution. We assume that this arises because of the known [14] lower quantum yield for the formation of $[\mathrm{Ru(bipy)_3}]^{+}$ at lower pH which probably in turn arises from less efficient quenching of $[\mathrm{Ru(bipy)_3}]^{2+*}$ by undissociated ascorbic acid than by ascorbate anion. Ascorbic acid is a weak acid (pK_a = 4.0) so that at low pH significant amounts of undissociated acid will be present in the solution.

Although we have not conclusively identified the reasons for the poor reproducibility of the photochemical reactions, we believe that traces of dissolved oxygen may be responsible. Support for this belief comes from the observation that addition of oxygen (1 cm^3) to the gas phase (33 cm^3) above a solution that had produced 0.088 cm^3 of hydrogen in 1 h dropped the rate of hydrogen production to 0.023 cm^3 h^{-1}. The role of the dissolved oxygen may be to react with [Ru-

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† This reaction, which is the subject of continuing studies, may be photochemical in nature.

‡ Although no data on the reversibility of this reaction are available, the high pressures involved suggest that the dimer will lose hydrogen under low pressures of hydrogen.

(bipy)$_3$]$^{2+*}$, or [Ru(bipy)$_3$]$^+$, or it may oxidise [PdH(PEt$_3$)$_3$]$^\cdot$ back to the palladium(II) cation. Either way, it is probable that dissolved oxygen is also responsible for the fact that the plot of rate of hydrogen production against concentration of [Ru(bipy)$_3$]$^{2+}$ does not pass through the origin. If so, it seems likely that one of the ruthenium species is being intercepted by O_2 rather than the palladium radical. Both [Ru(bipy)$_3$]$^{2+*}$ (ref. 1) and [Ru(bipy)$_3$]$^+$ (ref. 24) are known to be oxygen-sensitive.

Although exhaustion of [PdH(PEt$_3$)$_3$]$^+$ cannot be responsible for termination of the hydrogen-producing reaction, substantial bleaching of the [Ru(bipy)$_3$]$^{2+}$ occurs after long-term photolysis [Figure 4(*c*)]. In addition, a strong background signal, whose origin is unknown, also develops. It is not possible to decide whether the shoulder at *ca.* 490 nm arises from [Ru(bipy)$_3$]$^+$ or [Ru(H$_2$O)$_2$(bipy)$_2$]$^{2+}$ which is formed [14] on long-term photolysis of [Ru(bipy)$_3$]$^{2+}$ and ascorbic acid.

Clearly this bleaching accounts for the termination of the reaction but we also find that build-up of dehydroascorbic acid is a contributing factor. Thus, addition of dehydroascorbic acid (A) (Pd : A = 1 : 1.1) to a solution that had produced 0.093 cm^3 of hydrogen in 1 h totally inhibited hydrogen production and addition of a similar amount of dehydroascorbic acid to a fresh catalytic solution also gave the same result. A similar inhibition has previously been suggested [12] to be responsible for reaction termination in systems where cobalt(II) complexes act as electron relays.

Dehydroascorbic acid is a sufficiently strong oxidising agent [15,20] to oxidise [PdH(PEt$_3$)$_3$]$^\cdot$ to [PdH(PEt$_3$)$_3$]$^+$ in competition with protonation and/or further reduction. Apparently this reaction dominates if the concentration of dehydroascorbic acid is similar to that of [PdH(PEt$_3$)$_3$]$^+$.

Experimental

Phosphorus-31 n.m.r. spectra were recorded on a Brüker WM250 spectrometer operating in the Fourier-transform mode with proton-noise decoupling. U.v. spectra were recorded on a Pye-Unicam SP8-100 spectrophotometer and quantum yield measurements on a Jobin-Yvon fluorescence spectrometer. Hydrogen produced was analysed by g.l.c. on a Pye-Unicam 204 gas chromatograph using a glass column packed with type 5A molecular sieves with nitrogen as carrier gas and a katharometer detector.

All experiments were carried out under an atmosphere of oxygen-free nitrogen, which was not prepurified, using standard Schlenk-line and catheter-tubing techniques. All solvents were deaerated before use.

The complexes [M(PEt$_3$)$_3$] (M = Pt or Pd) were synthesised by standard literature methods [23] and buffer solutions (pH 6.88) were prepared from Na$_2$HPO$_4$ (0.25 mol dm^{-3}) and KH$_2$PO$_4$ (0.25 mol dm^{-3}); [PdH(PEt$_3$)$_3$]$^+$ solutions were prepared by dissolving [Pd(PEt$_3$)$_3$] in phosphate buffer at room temperature and stored under nitrogen. The concentrations of the complexes were determined gravimetrically as the PF$_6^-$ salts.[16]

(1) *General Photochemical Reactions.*—Solutions containing known amounts of [Ru(bipy)$_3$]$^{2+}$, [PdH(PEt$_3$)$_3$]$^+$, and ascorbic acid (0.7 mol dm^{-3}) were prepared under nitrogen and degassed by pumping until vigorous effervescence was observed and then introducing nitrogen. This process was repeated three times and the vessel was sealed. The solution was then photolysed with unfiltered light from a 500-W tungsten lamp as previously described.[25] For long-term irradiation, reactions were usually carried out with 5 cm^3 of solution in a 1-cm cylindrical cell fitted with a water jacket, through which water at ambient temperature was circulated. This cell was fitted with a septum for gas sampling, a greaseless tap for degassing, and a stopper. Hydrogen produced after a given time was sampled with a gas syringe and analysed by g.l.c. The reaction vessel was calibrated by injecting known volumes of pure hydrogen into the vessel containing buffer solution (5 cm^3), shaking and allowing to stand for 2 h before sampling with a gas syringe and analysing by g.l.c. U.v.–visible spectra taken of solutions during long term photolyses showed the presence of [Ru(bipy)$_3$]$^+$ ($\lambda_{max.}$ = 466 nm, lit.[26] 474—530 nm) [Figure 4(*b*)].

For kinetic experiments, reactions were carried out in a 1-cm quartz cell with similar attachments but no water jacket This was placed in a water-bath close to a quartz window through which the light passed; the temperature of the bath was held constant at 25 °C by a thermostatting circulating pump. Hydrogen sampling was carried out as described above.

(2) *Variation of Rate of Hydrogen Production with the Concentration of* [PdH(PEt$_3$)$_3$]$^+$.—Two solutions containing both [Ru(bipy)$_3$]$^{2+}$ (1.86×10^{-4} mol dm^{-3}) and ascorbic acid (0.7 mol dm^{-3}) were prepared, one in pure phosphate buffer, the other in phosphate buffer containing [PdH(PEt$_3$)$_3$]$^+$ (5.62×10^{-2} mol dm^{-3}). The solutions for photolysis were then prepared by transferring a known volume of the [PdH(PEt$_3$)$_3$]$^+$-containing solution to the degassed quartz cell, using a graduated pipette, and making the volume up to 2 cm^3 with the other solution. The whole solution was then degassed as described above and photolysed for 2 h.

(3) *Variation of the Rate of Hydrogen Production with the Concentration of* [Ru(bipy)$_3$]$^{2+}$.—Two solutions containing both [PdH(PEt$_3$)$_3$]$^+$ (2.81×10^{-2} mol dm^{-3}) and ascorbic acid (0.7 mol dm^{-3}) were prepared, one in pure phosphate buffer and the other in phosphate buffer containing [Ru(bipy)$_3$]$^{2+}$ (1.86×10^{-4} mol dm^{-3}). Solutions for photolysis were prepared by mixing these solutions and subsequent degassing as described above. The concentration of [Ru(bipy)$_3$]$^{2+}$ was checked spectrophotometrically ($\varepsilon_{450} = 1.45 \times 10^4$ dm^3 mol^{-1} cm^{-1}) [1] and the solution photolysed as described above.

(4) *Variation of the Quantum yield of Hydrogen Production with* pH.—Quantum yields were determined at 452 nm using the apparatus described above for use in kinetic experiments. Photolysis times were 2—3 h and gas sampling was as described above. The incident photon flux, determined by ferrioxalate actinometry,[27] was (1.0—1.5) $\times 10^{-7}$ einstein s^{-1} and the observed quantum yield was corrected for the fraction of [Ru(bipy)$_3$]$^{2+*}$ quenched by the ascorbate.[13]

The solutions were prepared by the slow addition of syrupy H$_3$PO$_4$ † to a solution of [PdH(PEt$_3$)$_3$]$^+$ (5.6×10^{-2} mol dm^{-3}) in phosphate buffer (30 cm^3) containing [Ru(bipy)$_3$]$^{2+}$ (1.86×10^{-4} mol dm^{-3}). The pH's of the solutions were measured under an atmosphere of N$_2$ using a pH meter. A 2-cm^3 portion of the solution was transferred to a degassed quartz cell containing ascorbic acid (0.245 g); the solution was degassed and photolysed as described above.

(5) *The Effect of Molecular Oxygen on the Rate of Hydrogen Production.*—A solution containing [Ru(bipy)$_3$]$^{2+}$ (*ca.* 2×10^{-4} mol dm^{-3}), [PdH(PEt$_3$)$_3$]$^+$ (5×10^{-2} mol dm^{-3}), and ascorbic acid (0.7 mol dm^{-3}) in phosphate buffer (2 cm^3) (pH 6.88) was photolysed in the kinetics apparatus described above for 1 h. Analysis of the gas showed hydrogen (0.088 cm^3) had been produced. The vessel was then degassed as described

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† For the lowest pH, *ca.* 0.5 cm^3 of H$_3$PO$_4$ was required so that changes in the concentration of [PdH(PEt$_3$)$_3$]$^+$ and [Ru(bipy)$_3$]$^{2+}$ have been ignored.

above and air (1 cm^3) was injected into the gaseous phase. After irradiation for a further hour, gas analysis showed that hydrogen (0.023 cm^3) had been produced.

(6) *The Effect of Dehydroascorbic Acid on the Rate of Hydrogen Production.*—(*a*) A solution prepared as described in (5) above was photolysed for 1 h; hydrogen (0.093 cm^3) was produced. Dehydroascorbic acid (0.019 g, 5.48×10^{-2} mol dm^{-3}) was added and the solution degassed. After photolysis for 1 h no further hydrogen was produced.

(*b*) This was carried out as in 6(*a*) above except that dehydroascorbic acid (0.02 g) was added to the initial solution. After photolysis for 1 h no hydrogen was produced.

Acknowledgements

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