Proflavine-sensitized Photoproduction of H_2 from Water with Electron-donors and a Colloidal Redox Catalyst

By KUPPUSWAMY KALYANASUNDARAM and MICHAEL GRÄTZEL
(*Institute of Physical Chemistry, Federal Institute of Technology,* 1015 *Lausanne, Switzerland*)

Summary Efficient photoproduction of H_2 from water in the presence of electron donors such as ethylenediaminetetra-acetic acid or triethanolamine and a colloidal Pt-redox catalyst, sensitized by proflavine, is reported; this is a two-component redox system for H_2 production as against the common three-component systems with an electron acceptor.

THERE has been considerable interest recently in the photoproduction of H_2 from water *via* visible light redox reactions as a means of solar energy conversion and storage.[1] In the last few years, several H_2-generating systems have been reported[2] and all these systems employ three principal components: a photosensitizer, an electron donor, and an electron acceptor with an additional redox catalyst to facilitate the gas production in solution. Systems involving fewer components are more practical and efficient overall and we report here a method of H_2 production using proflavine as the photosensitizer, ethylenediaminetetra-acetic acid (EDTA) or triethanolamine (TEOA) as the electron-donor, and a colloidal Pt redox catalyst. There have been several recent reports on three-component systems involving proflavine.[2a,3]

Visible light ($\lambda \geqslant 400$ nm) irradiation of aqueous solutions containing proflavine and electron donors such as EDTA (sodium salt) or TEOA in the presence of the colloidal redox catalyst Pt-PVA leads to the evolution of molecular H_2 gas. Typically, irradiation of 25 ml of aqueous solution buffered to pH 6·0, and containing proflavine ($2{\cdot}0 \times 10^{-5}$ mol l^{-1}), EDTA (sodium salt) ($1{\cdot}0 \times 10^{-2}$ mol l^{-1}), and 0·5 ml of colloidal Pt-PVA solution† leads to H_2 gas production at a rate of about 30 μmol l^{-1}. (Solutions were outgassed with argon prior to illumination and the H_2 gas produced was analysed on a Gow-Mac gas chromatograph on a molecular sieve 5A column.) Similar rates were obtained with TEOA (2×10^{-2} mol l^{-1}) as the electron-donor. The H_2 yields obtained show a significant dependence on the pH of the solution. Maximum H_2 yields were obtainable in the pH range 7·0—7·5 for TEOA and 5·0—6·0 for EDTA. Under optimal conditions, the H_2 yields from the two-component system are about a third less than those obtained if methyl viologen (concentration $\geqslant 10^{-3}$ mol l^{-1}) is also present in the irradiated solution. Concomitant with the H_2 gas production there are permanent spectral changes in the absorption spectrum of proflavine (Figure) depending on the amount of redox

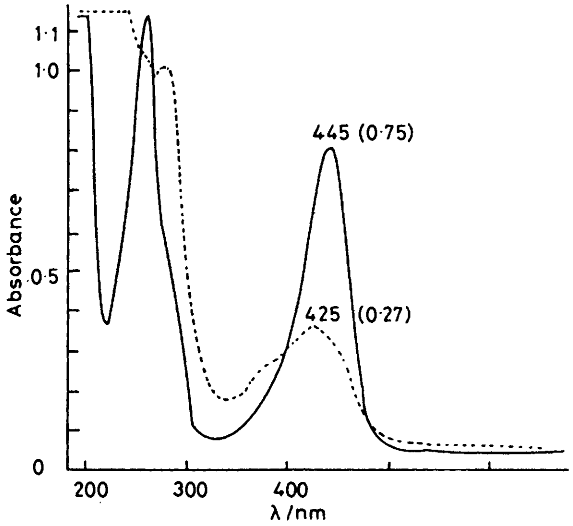

FIGURE.

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† The colloidal Pt solution, with Pt content *ca.* 2 mg/ml, was prepared according to earlier reported[4] procedures. Photolysis employed a 450 W Xe-arc lamp, with the lamp output filtered with a water filter and a 400 nm cutoff glass filter.

catalyst employed. The proflavine cation absorption (with maxima at 445 and 265 nm) shifts to 425 nm with an additional shoulder appearing at *ca.* 285 nm. The formation and characteristics of the photoreduction product absorbing at 425 nm have been examined by continuous and flash photolysis (reported in detail elsewhere[5]), and it is an irreversible photoproduct which accumulates in secondary reactions of the semi-reduced radical of the proflavine cation. There is slow, partial reversion to proflavine on letting air into these solutions. In the presence of methyl viologen (MV^{2+}) it has been shown that[3,5] MV^{2+} reacts rapidly and quantitatively with the semi-reduced radical ($PH\cdot$ or $P^{\cdot -}$) suppressing totally the build-up of any irreversible photoproducts. Even in the two-component redox system described above, if a ten-fold increase of redox catalyst solution is used there is no more formation of the 425 nm product with concomitant increase in the H_2 yields. The H_2 yields are about four times higher than those obtained at low concentration of the redox catalyst but are still less compared to those obtained when methylviologen is also used.

Mechanistically, the photoreactions leading to H_2 production and/or photoreduction of the proflavine cation can be summarised in reactions (1)—(6). Direct monitoring of the decay of the semi-reduced radical of the proflavine cation at its absorption maximum (λ 520 nm) by nanosecond ruby laser photolysis indicates that reaction (4) on the microelectrode surface of the redox catalyst is very efficient. The leuco-product is presumably a dimerisation product of $PH\cdot$ and not a radical. The pH dependence of H_2 production, with maximum yields at pH values close to the pK_a of the donors, arises, as in the three-component systems, from the differences in the reducing properties of various acidic and basic forms of the electron donors. According to the polarographic measurements of Kaye and Stonehill,[6] the redox potential for the one-electron-reduction couple ($P/P^{\overline{\cdot}}$) for proflavine is $-0\cdot78$ V(at pH 7·0). Hence the semi-reduced proflavine radical is a more powerful reducing agent than $MV^{\dot{+}}$ ($E_0' = -0\cdot44$ V) and as has been demonstrated here, in the presence of suitable redox catalysts, it itself is capable of directly reducing water to hydrogen. In many aspects, this system is analogous to the photoproduction of H_2 in the two-component system, triethylamine–$Ru(bipy)_3{}^{2+}$ (bipy = 2,2′-bipyridyl) in aqueous acetonitrile, when the photoreduced sensitizer $Ru(bipy)_3^+$ reduces water directly in the presence of the redox catalyst PtO_2.[7] Irreversible decomposition of the electron donors following oxidation is not necessary in experiments of this type. We have elsewhere demonstrated[8] that, with efficient colloidal redox catalysts (one for oxygen and one for hydrogen), it is possible to effect complete water decomposition in a totally reversible photoredox system $Ru(bipy)_3^{2+}$–methylviologen.

$$PH^+ \xrightarrow{h\nu} {}^1(PH^+)^* \longrightarrow {}^3(PH^+)^* \quad (1)$$

$${}^3(PH^+)^* + EDTA \longrightarrow PH\cdot + (EDTA)^{+\cdot} \quad (2)$$

$$PH\cdot \xrightarrow{-H^+} P^{\overline{\cdot}} \ (pK_a = 4\cdot5) \quad (3)$$

$$2P^{-\cdot} + 2H_2O \xrightarrow[\text{catalyst}]{\text{redox}} 2P + 2OH^- + H_2\uparrow \quad (4)$$

$$2PH\cdot \longrightarrow P + PH_2 \ (\text{acridane}) \quad (5)$$

$$PH\cdot \longrightarrow \text{leuco-product} \ (A_{425\ \text{nm}}) \quad (6)$$

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