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On a Novel System for the Photosensitized Water Reduction Which Contains the Iron-Sulfur Cluster, $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SBzl})_4]$

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A new system containing $\text{Ru}(\text{bpy})_3\text{Cl}_2$ and $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SBzl})_4]$ as a photocatalyst and a relay compound, respectively, was developed for hydrogen production from water by visible light irradiation. Studies on the effect of donors on the system clearly showed that EDTA was the most efficient among those investigated, and the hydrogen formation yields reached over 20000% with respect to both the photosensitizer and the iron-sulfur cluster. An interesting feature of the present system is the successful use of a ferredoxin model compound as a catalytic electron carrier.

Keywords—hydrogen evolution; ferredoxin model compound; photochemical water splitting; electron transfer reaction

The conversion of light energy into a chemical that is stable and can be harvested at will has attracted great interest in recent years. One promising approach to such goals is the photosensitized decomposition of water into its elements, which is of fundamental significance as a model for photosynthesis and also of practical interest for the production of hydrogen as a "clean" fuel. So far, work has been concentrated on the reduction half of the process,¹⁻⁶ using sacrificial electron donors, and comparatively few studies have been carried out on the oxidation side.⁷⁻¹¹

In such hydrogen-evolving system, light-driven electron transfer reactions have been exclusively examined employing trisbipyridineruthenium(II) (Ru^{2+}) and methyl viologen (MV^{2+}) as a photosensitizer and a relay compound, respectively, in the presence of platinum redox catalyst as shown in Chart 1.

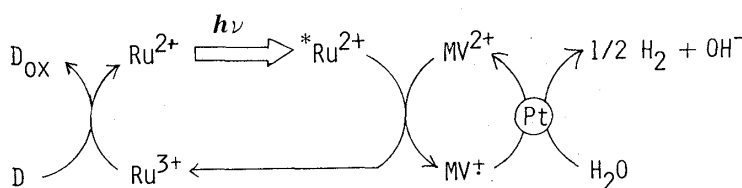
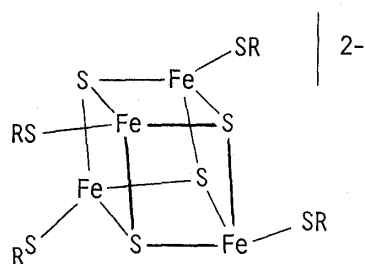


Chart 1

However, current reports^{3,12)} dealt with an inherent disadvantage of this device where the consumption of methyl viologen by platinum-catalyzed reduction of the aromatic rings with the hydrogen produced would take place to a significant extent, which makes the system become virtually inactive.

With respect to bioconversion of solar energy, on the other hand, it is widely accepted that the excited electron from photosystem I in plant photosynthesis travels down to a trap, which is probably bound ferredoxin, an iron-sulfur protein,¹³⁾ to free ferredoxin and nicotinamide adenine dinucleotide phosphate (NADP) reductase.¹⁴⁾ Several investigators have attempted to produce hydrogen by coupling of the photosynthetic electron flow of

Fig. 1. I (R = Bzl; abb. t^{2-})

isolated chloroplasts to bacterial hydrogenase.¹⁵⁻¹⁷ However, in recent years, the outstanding work on synthetic analogues of the active sites of the iron-sulfur and molybdenum-iron-sulfur proteins by Holm *et al.*^{13,18,19} has made it possible to apply "artificial ferredoxins" to organic synthesis as well as to simulate *in vivo* reactions.²⁰ Recent work has shown that such clusters can replace ferredoxin in a chloroplast-ferredoxin-hydrogenase H_2 -evolving system.^{21,22}

In these contexts, efforts to construct a totally synthetic device that is able to capture and store light energy using artificial ferredoxins seem to be of significance.

We describe here for the first time a novel system for the photochemically initiated production of hydrogen from aqueous solutions, based on the synthetic iron-sulfur compound I ($(Et_4N)_2[Fe_4S_4(SBzl)_4]$) (Fig. 1; abb. t^{2-}), which is comparatively stable and well characterized.^{23,24}

Experimental

Materials— $(Et_4N)_2[Fe_4S_4(SBzl)_4]$ was prepared as reported;²³ black plates, mp 123–124 °C, *Anal.* Calcd for $C_{44}H_{68}Fe_4N_2S_8$; C, 47.83; H, 6.20; N, 2.54; S, 23.21. Found: C, 47.44; H, 6.08; N, 2.33; S, 22.99. Water was purified by deionization, followed by distillation twice from all-glass apparatus. The following chemicals, obtained from the sources specified in parenthesis, were used as purchased: $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (Strem), K_2PtCl_4 (Kojima), and $RuO_2 \cdot 9H_2O$ (Alfa).

General Procedures for Preparation of Sample Solutions—A stock solution of Ru^{2+} in 0.1 M acetate buffer, pH 4.9, was diluted with the same solution or M/15 phosphate buffer to make up a desired concentration of the sensitizer. To prepare a 0.1 mM solution, for example, 1.5 ml of the Ru^{2+} stock (1.335 mM) was mixed with redox catalyst(s) and/or an electron donor, *N,N*-dimethylacetamide (DMA), to solubilize t^{2-} , and a buffer solution. The pH was recorded as an initial value at this point, and the solution was kept in a Pyrex flask equipped with a three-way stopcock through a taper of known total volume. It was then degassed by repeated evacuation and flushing with purified argon gas (freed from oxygen by passage through a hot tower containing Badische Anilin und Soda Fabrik Catalyst R3-11). An appropriate amount of t^{2-} in deaerated DMA was injected into this mixture *via* a Hamilton microsyringe. The whole was again degassed thoroughly as mentioned above. Thus, the final solution consisted of a 15 ml of buffer solution, 5 ml of DMA and the additives.

Illumination and Gas Analysis—The light source was a 400 W sunlight lamp (metal halide lamp; D400 or DR400 from Toshiba). Each irradiation was carried out on 20 ml of sample solution under an argon atmosphere. The Pyrex flask was placed approximately 3 cm in the case of the D400 and 10 cm for the DR400 from the lamp surface, and the solution was stirred magnetically during illumination. The temperature of the flask rose to 40–50 °C due to irradiation.

Hydrogen was detected by injecting 1 ml of degassed water into the flask (to maintain a positive pressure in the flask), removing 1 ml of the gas, and injecting it into a Shimadzu GC-4APFE gas chromatograph equipped with a 2 m × 3 mm molecular sieve 13X column. Argon was used as a carrier gas, the column temperature was 35 °C, and hydrogen was determined with a thermal conductivity detector (filament current 90 mA). The composition of the gas was measured quantitatively with a Shimadzu Chromatopac-EIA data analyzer. The response to hydrogen was linear over the range from 45 nmol to 45000 nmol used for the analysis.

Results and Discussion

Influence of Donors on Hydrogen Evolution

The importance of the iron-sulfur cluster in this system is clear from Fig. 2; both the rate

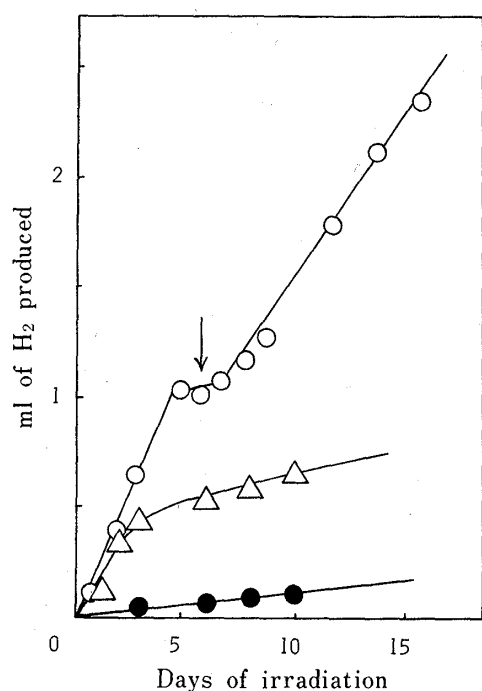


Fig. 2. Effect of $\text{Fe}_4\text{S}_4(\text{SBzl})_4^{2-}$ on Hydrogen Generation

In the presence of EDTA with 0.1 mM $\text{Ru}(\text{bpy})_3\text{Cl}_2$; ratios of t^{2-}/Ru^{2+} were 1.0 (○), 0.1 (△), and zero (●). Further addition of t^{2-} is indicated by the arrow. See ref. 25.

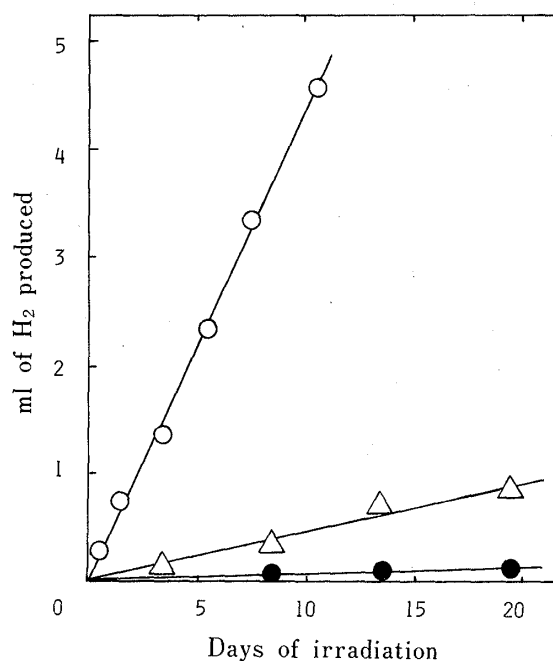


Fig. 3. Production of Hydrogen in the Presence of Donors as a Function of Time

Ru^{2+} (0.1 mM) / t^{2-} (0.1 mM) / K_2PtCl_4 (0.52 mM) with EDTA (○), Cys (△), and TEOA (●).

TABLE I. H_2 Production with Various Donors^{a)}

Donor	pH	$r_{\text{H}_2}^b$	$V_{\text{H}_2}^c$
EDTA	4.2	21800	969
Cysteine	4.3	2470	94
TEOA	6.7	440	15
Asc	4.4	50	2
EDTA ^{d)}	5.0	262	12
EDTA ^{e)}	4.2	550	26

a) Ru^{2+} (0.1 mM)/ t^{2-} (0.1 mM)/ K_2PtCl_4 (0.52 mM).

b) H_2 formation rate in $\mu\text{l} \cdot \text{d}^{-1} \cdot \text{l}^{-1}$. c) H_2 yield in $\mu\text{mol} \cdot \text{d}^{-1} \cdot \text{l}^{-1}$.

d) Without K_2PtCl_4 . e) t^{2-} was omitted.

and yield of hydrogen formation in the presence of the Fe-S chelate were twenty times higher than those without t^{2-} , as discussed in our preliminary account.²⁵⁾

Examinations of the effect of electron donors on hydrogen generation were carried out by illuminating 20 ml of a solution consisting of Ru^{2+} (0.1 mM), t^{2-} (0.1 mM) and K_2PtCl_4 (0.52 mM) under argon. The donors tested include triethanolamine (TEOA), ethylenediaminetetraacetic acid (EDTA), ascorbic acid (Asc) and cysteine (Cys). Upon irradiation of the above mixture, continuous evolution of hydrogen was observed, and the efficiency depended largely on the donor employed. The initial rate of H_2 formation per day per liter of solution (r_{H_2} : $\mu\text{l} \cdot \text{d}^{-1} \cdot \text{l}^{-1}$) with EDTA as an electron donor was fifty times faster than that with TEOA, and other compounds were much slower. The best yield of H_2 per day per liter of solution (V_{H_2} : $\mu\text{mol} \cdot \text{d}^{-1} \cdot \text{l}^{-1}$) was also obtained with EDTA; the yield was sixty-five times

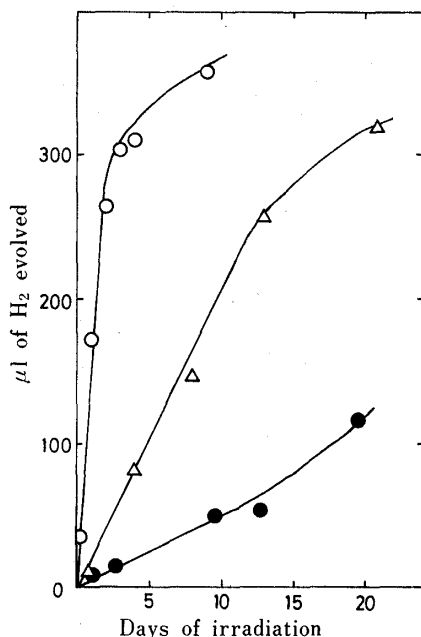


Fig. 4. Effect of Concentration of the Photosensitizer on H₂ Production

Ru²⁺: 0.1 mM (○), 1.0 mM (△), and 10 mM (●).
See the text for further details.

higher than that of TEOA. Furthermore, it turned out that the numbers of catalytic cycles²⁶⁾ in the case of EDTA were over 200 for both the photosensitizer and ferredoxin model compound, indicating that the reaction proceeded catalytically. Irradiation of a solution without either the Fe-S cluster or redox Pt catalyst gave little hydrogen. These results are summarized in Table I.

A good linear relation between hydrogen yield and time of irradiation was observed. The yield reached 36% with respect to EDTA, amounting to 4.55 ml of hydrogen, after 10 d, as illustrated in Fig. 3, which also shows the effect of various donors.

The Photoreactions in the Absence of Extra Donors

We have demonstrated that the pH of the reaction medium markedly influences hydrogen formation. The optimum pH was found to be 4 to 5, and the rate of H₂ formation decreased as the solution became more basic, being ten times slower at pH 9 than at pH 5. It has also been proved that the protons are from water by means of an experiment conducted in deuterium oxide.²⁵⁾ The reaction below pH 4 has not been examined, since the cluster seems to be insufficiently stable in this region.

When Ru²⁺ (0.1 mM) and t²⁻ (0.1 mM) in 0.1 M acetate buffer at pH 5 were irradiated in the presence of redox catalysts, K₂PtCl₄ (0.51 mM) and RuO₂·9H₂O (0.56 mM), continuous hydrogen production was observed. The yields with respects to Ru²⁺ and t²⁻ reached 1600% ($r_{\text{H}_2} = 8600 \mu\text{l} \cdot \text{d}^{-1} \cdot \text{l}^{-1}$; $V_{\text{H}_2} = 89 \mu\text{mol} \cdot \text{d}^{-1} \cdot \text{l}^{-1}$). A higher yield of 2900% with respect to t²⁻ was obtained with 0.05 mM t²⁻ ($r_{\text{H}_2} = 3000$, $V_{\text{H}_2} = 103$). The effect of redox catalysts was clear; the rate of H₂ formation decreased to one-sixtieth in the absence of a catalyst ($r_{\text{H}_2} = 150$, $V_{\text{H}_2} = 6$).

When water itself acts as both an electron donor and acceptor, on the other hand, oxygen equivalent to half the volume of H₂ should be produced. In the experiment with 0.1 mM Ru²⁺ and 0.1 mM t²⁻, gas chromatographic analysis showed the presence of 17.5 μl of oxygen and 34.6 μl of hydrogen after the first 6 h of illumination. However, the subsequent increase of oxygen production was less than expected.

When oxygen evolution was examined with a model system using pentaammine chlorocobalt(III) as an electron acceptor,⁸⁾ a rapid decrease of oxygen generated was observed after one day under the conditions employed, which suggests that side reactions of the oxygen occur. Further work is in progress and will be reported later.

The lowest concentration of photosensitizer among the three investigated gave the best H_2 formation, as shown in Fig. 4. In higher concentrations, back reactions (self-quenching) and/or saturation behavior²⁾ may retard the reaction. These effects should be related to the potentials involved as well as to mechanistic factors. Little H_2 was produced in the absence of t^{2-} ($r_{H_2} = 90$, $V_{H_2} = 5$) or Ru^{2+} ($r_{H_2} = 230$, $V_{H_2} = 5$).

In conclusion, we have developed a novel system for the photochemical splitting of water in which a synthetic ferredoxin analogue plays a key role, probably as an electron carrier. It may be possible to modify the photosensitizer or to use mixtures of sensitizers so as to cover the visible spectrum as well as possible and to increase the efficiency of light harvesting. It has been shown that a series of porphyrins are potent alternatives in the present device.²⁷⁾ The physical separation of the reaction species as in systems involving micellar phases, vesicles or solid surfaces, and the use of other kinds of Fe-S compounds^{13,19)} are also attractive possibilities.

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