Light-induced hydrogen production using waste compounds as sacrificial electron donors

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Abstract. Systems for the conversion and chemical storage of solar energy are usually based on photo-induced electron transfer reactions from an excited sensitizer to an electron acceptor (i.e. an electron relay compound). We have investigated the photo- and electrochemical properties of two novel electron relay compounds: 1,1'',1'''-trimethyl[4,2'; 4',4''; 6',4'''']quaterpyridinium trichloride (**1**) and 1,1',1'',1'''-tetramethyl[4,2'; 4',4''; 6',4'''']quaterpyridinium tetrachloride (**2**). When solutions containing Ru(bpy)₃Cl₂ or Zn-porphyrin (as photosensitizer), compound **1** or **2** and EDTA (as sacrificial electron donor) are irradiated by visible light ($\lambda > 400$ nm), only the formation of reduced relay compound **1** occurs. Addition of platinum catalyst to such solutions with compound **1** leads to the formation of hydrogen. Quantum yields are in the range of 5%, calculated for absorbed light. Using other sacrificial electron donors such as alcohols or glucose (or waste compounds like 4-chlorophenol) did not result in hydrogen evolution. However, **1** and **2** are reduced by these sacrificial electron donors in the absence of an additional photosensitizer, when near UV irradiation light ($\lambda > 280$ nm) is used. Quantum yields for hydrogen production with compound **1** are about 2%, calculated for absorbed light out of GC-measurements from H₂ in the gas phase above the irradiated solution. The photo- and electrochemical properties of compounds **1** and **2** are discussed.

Keywords. Electron transfer; photo-induced hydrogen production; radicals; electron relays; relay sensitizer.

1. Introduction

Conversion and chemical storage of solar energy has become more interesting since problems of environmental pollution and greenhouse warming increased. Different approaches have been made for the conversion of light. Besides the production of hydrogen by photovoltaic cells (generating electricity), combined with the electrolysis of water, direct hydrogen production by the direct light driven splitting of water has attracted much attention (Harriman and West 1982; Pelizzetti and Schiavello 1991).

Such systems are based usually on photo-induced charge separation.

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After excitation (1) a photosensitizer (S^*) releases an electron (2) to an electron-accepting molecule (electron relay, R) or receives an electron (3) from an electron donor (D).

In the presence of a suitable catalyst (e.g. platinum) the reduction of water can be achieved either by the reduced relay radical R^- or the reduced sensitizer A^- to give H_2 :

The reduction of the oxidized sensitizer S^+ (or the oxidized electron donor D^+) can be done either by oxidizing water to oxygen (5) or in the presence of a sacrificial electron donor D. In this case, the oxidation of the electron donor is irreversible in reaction (3) or (6):

For practical applications, the use of sacrificial electron donor is of interest, only if it is cheap or a waste product of some other reaction.

The utilization of a (organic) compound as such a donor is strongly limited by the redox potentials of the sensitizer in its ground and excited state(s).

Since the oxidation potentials of widely used sensitizers (e.g. $Ru(bpy)_3^{2+}$: $E_0^{2+/3+} = 1.27$ V, $E_0^{+/2+} = 0.8$ V vs. NHE) lie in the region of +1.5 V, we tried to find other substances with more positive oxidation potentials (in their excited states).

2. Experimental details

Compounds **1** and **2** (see figure 1) were prepared according to Eichinger *et al* (1987) and Bauer and Königstein (1991). *Tris* (2,2'-bipyridyl) ruthenium(II)chloride. $6 H_2O$ ($= Ru(bpy)_3^{2+}$, Janssen) and methyl viologen ($= MV^{2+}$, Aldrich) were used without further purification.

Figure 1. Compounds **1** and **2**: **1**. $R = -CH_3$, $R' = -$, $x = 3$; **2**: $R = R' = -CH_3$; $x = 4$.

H₂-production: Argon-purged solutions [containing 1 ml relay (compound 1 or 2, $c_0 = 10^{-2}$ mol/l), 0.5 ml acetate buffer ($c_0 = 1$ mol/l), 1 mol sacrificial electron donor (EDTA, 2-propanol or glucose, $c_0 = 0.1$ mol/l), 0.3 ml Pt-catalyst ($c_0 = 109$ mg/l prepared according to Bauer and Königstein (1991)) and 0.2 ml water] were irradiated by a Hg high pressure lamp (photon flux: $I_0 = (2.1 \pm 0.2) \times 10^{16}$ photons $s^{-1} cm^{-2}$, calculated from 280 to 580 nm, measured by ferrioxalate actinometry).

Solutions with $Ru(bpy)_3^{2+}$ or proflavine as sensitizer consisting of 0.3 ml sensitizer ($c_0 = 5 \times 10^{-3}$ mol/l), 0.6 ml relay (methyl viologen, compound 1 or 2, $c_0 = 10^{-2}$ mol/l), 0.5 ml acetate buffer ($c_0 = 1$ mol/l), 0.5 ml 2-propanol, 0.3 ml platinum catalyst ($c_0 = 109$ mg/l) and 0.8 ml water were irradiated with visible light (400 nm cut-off-filter, 250 W-tungsten halide filament lamp, photon flux: $I_0^{400-580\text{ nm}} = (3.33 \pm 0.05) \times 10^{17}$ photons $s^{-1} cm^{-2}$).

The H₂-concentration in the gas phase was determined by GC-analysis (Carlo Erba Instruments: GC 6000, with HWD-detector 430, column: 2 m packed iron steel column, filled with 5 Å molecular sieve, carrier: N₂(99.999%)).

Spectroscopy and fluorescence: All absorption spectra were recorded with a Hitachi 220 spectrophotometer. Fluorescence and excitation spectra were monitored with a Perkin Elmer LS 50 fluorescence spectrophotometer. As solvents, water (twice distilled) and acetonitrile (p.A.) were used. The concentration was 10^{-3} mol/l, in acetonitrile BF_4^- was used as counter ion (instead of Cl^-).

Cyclovoltammetry: Measurements with compound 1 were reported in Bauer *et al* (1992); those of 2 were done with a Polarograph VA663 (Metrohm AG) equipped with a Scanner VA E612 and Polarecord E506 reference electrode: Ag/AgCl; acetonitrile solution (working electrode: hanging mercury drop); supporting electrolyte: (0.1 mol/l tetrabutyl ammonium perchlorate (TBAP, electrochemical grade), concentration of compound 2: $c = 2 \times 10^{-4}$ mol/l; scan speed: $v_s = 50$ mV/s–200 mV/s).

3. Results and discussion

Out of phosphorescence measurements the 0–0 transition energy of $Ru(bpy)_3^{2+}$ is calculated to be 2.1 eV. With its ground state redox potentials at $E_0^{2+/3+} = +1.27$ V vs. NHE, and $E_0^{+/2+} = +0.8$ V vs. NHE, those of the excited triplet state are $E_0^{2+*/3+} = 0.84$ V and $E_0^{+/2+*} = 0.84$ V (vs. NHE) (Juris *et al* 1988). So the maximum oxidation power of $Ru(bpy)_3^{3+}$ is 1.27 V (in the ground state). Only a small number of organic compounds (soluble in water) are known, which can be oxidized at this potential (e.g. EDTA, triethanol amine,...). Alcohols, acids (Kolbe photoreaction!) need a more positive potential for their use as sacrificial electron donor agents.

Light-induced hydrogen production experiments with aqueous solutions of $Ru(bpy)_3^{2+}$ (as photosensitizer), methyl viologen (MV^{2+}) or compound 1 (as electron relay substance), platinum catalyst, acetate buffer and EDTA gave H₂ with quantum yields of 15 and 4% for MV^{2+} and 1, respectively (calculated for absorbed light, Bauer and Königstein 1991, 1993). Using compound 2 instead of MV^{2+} or 1 as electron relay compound, no H₂ could be produced. Since the first reduction potential of 2 ($E_0^{(2)} = -1.15$ V vs. NHE, see table 1) is more negative than that of $Ru(bpy)_3^{2+*}$ ($E_0^{2+*/3+} = -0.84$ V vs. NHE) no electron transfer can occur from the excited sensitizer to the electron relay according to (2).

Table 1. Data on compounds **1** and **2**.

Relay sensitizer compound	$\lambda_{\text{max}}^{f1}$ [nm]	$E_{\text{pH}=0}$ [mV]	dE/dpH [mV]	$E^{R+/R3+*}$ [V]	ΔE^{0-0} [eV]	$\Phi_{(1/2)\text{H}_2}$ [%]
1	372	−344	−24	2.87	3.33	2
2	434	−1150*	—	1.71	2.86	—

$E_{\text{pH}=0}$ extrapolated values from Bauer and Königstein (1991); all potentials vs. NHE;

dE/dpH measured with CV at different pH values (pH = 3–13) (Bauer and Königstein 1991); $E_{\text{pH}} = E_{\text{pH}=0} + \text{dE/dpH} \times \text{pH}$;

$\lambda_{\text{max}}^{f1}$ maximum of fluorescence emission;
 $E_0^{R+/R3+*}$ redox potentials (pH = 7) of the excited states for the reaction:
 $R^{3+*} + 2e^- \rightarrow R^+$;

ΔE^{0-0} zero-zero transition energy, calculations from $\lambda_{\text{max}}^{f1}$;

$\Phi_{(1/2)\text{H}_2}$ quantum yields for H_2 production (for absorbed light, from 280–360 nm);

* electrochemical measurements of compound **2** were performed in acetonitrile in the absence of protons.

Hydrogen production experiments with other organic sacrificial electron donors (e.g. 2-propanol, glucose, 4-chlorophenol) failed due to unsuitable redox potentials, as described above.

We have shown earlier (Bauer and Königstein 1990, 1991, 1993) that 1,1'',1'''-trialkyl [4,2';4',4'';6',4'''] quaterpyridinium trichlorides can act both as photosensitizers and electron relays when excited by near UV light ($\lambda > 280$ nm). Excitation maxima in aqueous solutions for compound **1** were found at 300 and 340 nm (Eichinger *et al* 1987; Bauer and Königstein 1991).

Fluorescence measurements of aqueous solutions of **2** ($c = 10^{-3}$ mol/l, counter ion: ClO_4^-) gave emission maxima at 370, 569 and 722 nm. Excitation maxima for the luminescence at 370 nm could be observed at 346 nm and for the yellow green emission (569 nm) at 392 and 460 nm (figure 2).

The results are in good agreement with those obtained for other derivatives in the series of the 1,1'',1'''-trialkyl [4,2';4',4'';6',4'''] quaterpyridinium trichlorides (Eichinger *et al* 1987; Bauer and Königstein 1991).

Emission properties of both compounds **1** and **2** in acetonitrile were a little different from the results in aqueous solutions, reported above. An additional emission band appears at 427 nm (**1**) and 429 nm (**2**) with excitation maxima at 367 nm (**1**) and 378 nm (**2**) (see figure 3).

Electrochemical measurements of **2** in acetonitrile gave as a result two reversible reduction steps at −1.15 and −1.33 V (vs. NHE). The shift to more negative potentials compared with **1** is attributed to the fourth methyl group in **2**.

Calculating the 0–0 transition energies out of the fluorescence measurements (Juris *et al* 1988) of aqueous solutions (see figure 2 and table 1), we found $\Delta E^{0-0} = 3.33$ and 3.35 eV for **1** and **2**, respectively. The redox potentials of their excited states are obtained with their ground state redox potentials of $E_0^{(1)} = -0.51$ V (vs. NHE, pH = 7), and $E_0^{(2)} = -1.15$ V (vs. NHE) from cyclic voltammetry (CV): $E_0^* = +2.82$ and $+2.20$ V (vs. NHE) for **1** and **2**, respectively (see table 1). This is much more positive than the potential which can be reached by $\text{Ru}(\text{bpy})_3^{2+}$.

Figure 2. Fluorescence (—) and excitation spectra (-----) of compounds **2** in water.

Figure 3. Fluorescence (—) and excitation spectra (-----) of compounds **2** acetonitrile.

Excitation of aqueous solutions, containing compound **1** or **2**, phosphate buffer ($pH = 7$) and a sacrificial electron donor (EDTA, glucose or 2-propanol), with near UV light ($\lambda > 280$ nm) resulted in the formation of reduced relay molecules and the oxidation of organic compounds. In contrast, $Ru(bpy)_3^{2+}$ was successfully used as photosensitizer only in combination with EDTA as sacrificial electron donor.

In the presence of a platinum catalyst hydrogen could be detected in the gas phase above the solution. The quantum yield was calculated for absorbed light to be: $\Phi_{(1/2)H_2} = 2\%$ for compound **1**. However compound **2** was not able to produce H_2 under these conditions.

Using waste water containing 100 ppm 4-chlorophenol as sacrificial electron donor agent for photoinduced H_2 -formation with compound **1** or **2** did not succeed, although thermodynamically allowed.

A high excess of the electron-donating substance is necessary to obtain sufficiently fast reaction rates. In case of glucose and 2-propanol the initial sacrificial donor concentration was five times the concentration of **1** and **2**, respectively.

4. Conclusion

Both compounds **1** and **2** were found to be able to undergo reversible redox processes. The first reduction potentials were determined by cyclic voltammetry $E_0 = -0.51$ and -1.15 V (at pH = 7, vs. NHE) for **1** and **2**, respectively. Fluorescence measurements of aqueous solutions showed that both compounds gave blue luminescence emission with its maxima at 372 nm (**1**) and at 370 nm (**2**), when excited by near UV-light ($\lambda^{\text{Ex}} = \sim 340$ nm). With 0–0 transition energies (from the emission properties) of 3.33 (**1**) and 3.35 eV (**2**), redox potentials of the excited states were calculated: $E^{*(1)} = 2.82$ V and $E^{*(2)} = 2.20$ V (pH = 7, vs. NHE). These values are much more positive than the redox potentials of $\text{Ru}(\text{bpy})_3^{2+}$ (0.8 V excited or 1.27 V ground state vs. NHE, respectively). Hydrogen production experiments showed that organic compounds in excess can act as sacrificial electron donors with **1** or **2** (as relay-sensitizers).

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References

- Bauer R, Hofstadler K and Königstein Ch 1992 *Proc. Indian Acad. Sci. (Chem. Sci.)* **104** 265
- Bauer R and Königstein Ch 1990 in *Hydrogen energy progress VIII* (eds) T N Veziroglu and P K Takahashi (New York: Pergamon)
- Bauer R and Königstein Ch 1991 *J. Photochem. Photobiol.* **A59** 61
- Bauer R and Königstein Ch 1993 *Int. J. Hydrogen Energy* **18** 205
- Eichinger K, Nussbaumer P and Vytlačil R 1987 *Spectrochim. Acta* **A43** 731
- Harriman A and West M A (eds) 1982 *Photogeneration of hydrogen* (London: Academic Press)
- Juris A, Balzani V, Barigelli F, Campagna S, Belser P and von Zelewsky A 1988 *Coord. Chem. Rev.* **84** 85
- Pelizzetti E and Schiavello M (eds) 1991 *Photochemical conversion of solar energy* (Amsterdam: Kluwer)