Homogeneous Photoredox System for Hydrogen Production by Solar Energy

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In a redox system consisting of 5×10^{-5} mol dm^{-3} $Ru(bpy)_3^{2+}$complex, 4×10^{-3} mol dm^{-3} methylviologen and 5×10^{-3} mol dm^{-3} EDTA in aqueous solutions (pH = 3 to 8.5) without catalyst, hydrogen is formed under illumination with light $\lambda > 360$ nm. The highest yield was established in the pH-range between 4 and 5. The degradation of the components by prolonged use was studied spectroscopically. For comparison hydrogen evolution was also studied replacing EDTA by TEA or SCN^-, respectively, in the above mentioned system.

1. Introduction

Various attempts have been made in the last years in order to develope suitable redox systems for photochemical utilization of solar energy. Thereby special attention has been paid to ruthenium-bipyridil-complexes as a suitable mediator for photon energy in such devices [1—4]. Using monolayer films of $Ru(bpy)_3^{2+}$ derivatives immersed in water, hydrogen evolution under illumination was reported [5]. Subsequently, however, these observations could not be reproduced [6—9]. Recently, it has been demonstrated that with ruthenium-trisbipyridil ($Ru(bpy)_3^{2+}$), applied as a photosensitizer in combination with a suitable electron acceptor (e.g. methylviologen, MV^{2+} [10, 11] or a rhodium-bipyridil complex [12, 13]) and an electron donor (e.g. triethanolamine, TEA [11, 12] or EDTA [10]) in aqueous solutions, hydrogen is produced under illumination with light of $\lambda > 400$ nm. A catalyst, such as PtO_2 (Adam's catalyst) [11], colloidal Platinum [10] or in situ generated Pt [12] was always necessary to promote the reaction of H_{aq}^+ with the reduced electron acceptor leading to hydrogen formation. The yields were strongly pH dependent and the maximum value of 3.6×10^{-4} H_2 mol dm^{-3} h^{-1} was obtained at pH = 7, applying a 450 W Xe-lamp and a cut-off filter for $\lambda < 400$ nm [11]. Other authors found 2.3×10^{-3} H_2 mol dm^{-3} h^{-1} at pH = 5 (light $\lambda > 400$ nm) [10] and 4.5×10^{-3} H_2 mol dm^{-3} h^{-1} at pH = 7.5 (150 W halogen lamp [13]). In all cases a degradation of the substrates in the solution was observed. Thereby turnover numbers were determined to be 10 for MV^{2+} and 100 for $Ru(bpy)_3^{2+}$ [10] in one case and 150 for the Rh-complex and 2300 for $Ru(bpy)_3^{2+}$ in a second case [13]. Those for the electron donor (TEA or EDTA) were near unity.

The reduced form of methylviologen, namely $M\dot{V}^+$ [14, 15], is of special interest, as its redox potential ($E^0 = -0.44$ V [16] or $E^0 = -0.466$ V [17]) is negative enough to reduce water to hydrogen. On the other hand, according to the previously presented reaction mechanism, a degradation of the electron donor occurs [10—13]. This fact, however, is of basic importance regarding a practical use of such systems. Hence, experiments with a system consisting of $Ru(bpy)_3^{2+}$, MV^{2+} and EDTA without catalyst were designed in order to examine the stability of the substrates and the efficiency of the hydrogen production. In this case the blue coloured radical cation, $M\dot{V}^+$, should also become electronically excited under the applied steady-state conditions and its reactivity will be essentially enhanced. In addition to this PtO_2 was added as a catalyst to the same system to check its influence. Further it was attempted to replaced the amine, acting as an electron donor, by a regenerable inorganic substrate.

2. Experimental

$Ru(bpy)_3^{2+}$ was synthesized from $RuCl_3$ and 2,2′-Dipyridil [18]. 2,2′-Dipyridil (Koch-Light, Coinbrook, England), methylviologen (BDH Chemicals Ltd., Poole, England) and all other chemicals (Merck, Darmstadt, FRG) were of analytical grade and used without further purification. The solutions

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were prepared with 4 times distilled water. A double wall irradiation vessel ($d = 2,8$ cm, $l = 6$ cm, containing 30 ml solution) was connected with a thermostat. The solutions of: 5×10^{-5} mol dm^{-3} $Ru(bpy)_3^{2+}$, 4×10^{-3} mol dm^{-3} MV^{2+}, 4×10^{-3} mol dm^{-3} EDTA, or 5×10^{-2} mol dm^{-3} SCN^- or 5×10^{-2} mol dm^{-3} TEA were saturated for about 1 h with high purity argon (Messer Griesheim, Vienna). The pH values were adjusted with $HClO_4$ or NaOH. The irradiations were performed with a 450 W Xe-lamp (Oriel), equipped with a 10 cm IR-water filter and a cut-off glass filter for $\lambda < 360$ nm.

The produced hydrogen was collected by means of a vacuum line and determined by gas chromatography (Fractovap, 116 E, molecular sieve 5 Å, Perkin Elmer).

3. Results

3.1. *Photochemical Behaviour of $Ru(bpy)_3^{2+}$ in Aqueous Solution*

It is supposed that unlike many metal complexes, $Ru(bpy)_3^{2+}$ does not readily undergo the photochemical loss of ligands [4]. In order to check its stability, absorption spectra of 5×10^{-3} mol dm^{-3} $Ru(bpy)_3^{2+}$ were measured in aqueous solutions at $pH = 6.5$ prior to and after illumination for up to 6 hours. The change of the optical density ($OD \cdot cm^{-1}$) for several irradiation periods is presented in Figure 1.

3.2. *The Ru-complex/TEA/MV^{2+} System (with Catalyst)*

The photochemical formation of hydrogen by illuminating the homogeneous aqueous system consisting of $Ru(bpy)_3^{2+}$, MV^{2+}, and TEA [11] was reinvestigated for comparison. This was necessary because the photochemical results in general strongly depend upon irradiation geometry, light intensity and other factors. A solution of 5×10^{-5} mol dm^{-3} $Ru(bpy)_3^{2+}$, 4×10^{-3} mol dm^{-3} MV^{2+}, and 5×10^{-2} mol dm^{-3} TEA in the presence of 10–20 mg PtO_2 ($pH = 6.7$) was illuminated under stirring for various periods. The amount of hydrogen evolved for the first 2 h of irradiation was less than observed by other authors [11]. This discrepancy is due to the above mentioned factors. After prolonged irradiation the hydrogen yields decrease substantially. Mean values for various irradiation periods are given in Table 1, series Nr. 1.

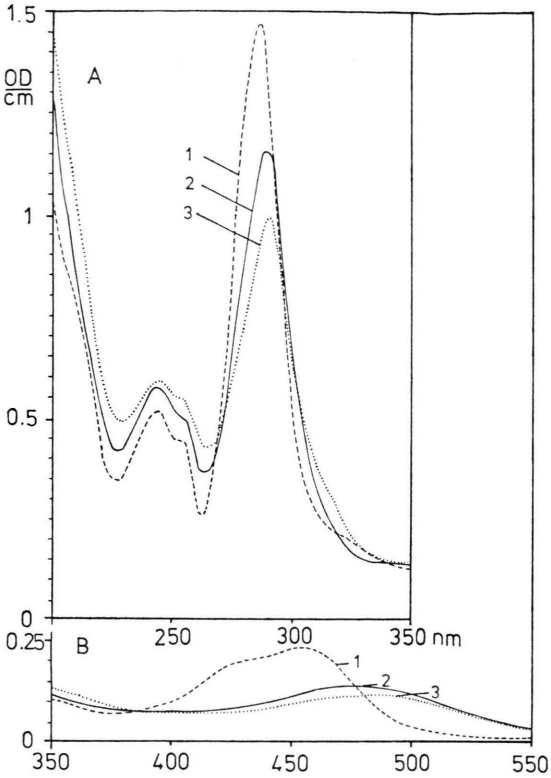

Fig. 1. Absorption spectra 5×10^{-5} mol dm^{-3} $Ru(bpy)_3^{2+}$ complex before and after illumination ($\lambda > 360$ nm) in aqueous solutions at $pH = 6.5$ ($A = 200$ to 350 nm, $B = 350$ to 550 nm): non-irradiated (1), irradiation time 2 h (2) and 6 h (3).

Table 1. Hydrogen evolution by illuminating ($\lambda > 360$ nm) photoredoxsystems containing $Ru(bpy)_3^{2+}$ in aqueous solutions, pH = 6.7.

Nr.	System	$\times 10^{-5}$ mol dm^{-3} H_2 obtained by irrad. times of:		
		2 h	4 h	6 h
1	$5 \cdot 10^{-5}$ m $Ru(bpy)_3^{2+}$ $4 \cdot 10^{-3}$ m MV^{2+} $5 \cdot 10^{-2}$ m TEA with PtO_2	8	9.7	9.8
2	$5 \cdot 10^{-5}$ m $Ru(bpy)_3^{2+}$ $4 \cdot 10^{-3}$ m MV^{2+} $5 \cdot 10^{-2}$ m TEA (without catalyst)	16	28	31.8
3	$5 \cdot 10^{-5}$ m $Ru(bpy)_3^{2+}$ $4 \cdot 10^{-3}$ m MV^{2+} $5 \cdot 10^{-2}$ m SCN^- (without catalyst)	0.2	–	–

Additionally, it was of practical interest to investigate the photochemical stability of the system under prolonged irradiation conditions. A strong change of the absorption spectra at 260 and 450 nm taken as a function of irradiation time indicated an essential degradation process.

3.3. *Ru-complex/TEA/MV^{2+} System without Catalyst*

In order to obtain some more information about the effect of the catalyst in this system, experiments in its absence were carried out under otherwise unchanged conditions. The obtained hydrogen yields are much higher and are presented as series Nr. 2 in Table 1. The absorption spectrum after illumination for 6 h showed only a decrease of the OD-values in the range of 400—470 nm, due to the degradation of the Ru-complex.

3.4. *SCN$^-$ as an Inorganic Electron Donor*

An attempt was made to substitute the electron donor TEA or EDTA by 0.05 mol dm^{-3} SCN$^-$. All other compounds as well as irradiation conditions were kept unchanged. No catalyst was used in this system. At an irradiation time of 45 min ($pH = 6.5$) a relative small hydrogen yield was found (Table 1, series Nr. 3). It might be mentioned that in this case only a slight change of the absorption spectrum was observed after irradiation.

3.5. *The Ru-complex/EDTA/MV^{2+} System (without Catalyst)*

In analogy to the previously described systems, solutions in which TEA was replaced by 4×10^{-3} mol dm^{-3} EDTA were irradiated under the same conditions at $pH = 3$ to 8.5. No catalyst was used in this case. The mean H$_2$-yields of several measurements (irradiation time 45 min) are summarized in Table 2. The absorption spectra measured before and after various irradiation times are shown in Figure 2.

Table 2. Photochemical formation of hydrogen as a function of pH at 25°C. Aqueous solutions of: 5×10^{-5} mol dm^{-3} Ru(bpy)$_3^{2+}$, 4×10^{-3} mol · dm^{-3} MV$^+$ and 4×10^{-3} mol dm^{-3} EDTA.

pH	H$_2$-yield $\times 10^{-4}$ mol dm^{-3} · h^{-1}
3.0	2.6
3.7	2.7
4.0	4.1
4.7	6.6
5.0	3.9
6.0	1.9
7.0	1.3
8.5	0.5
4.6*	11.0

* 10 mg of PtO$_2$ added before illumination.

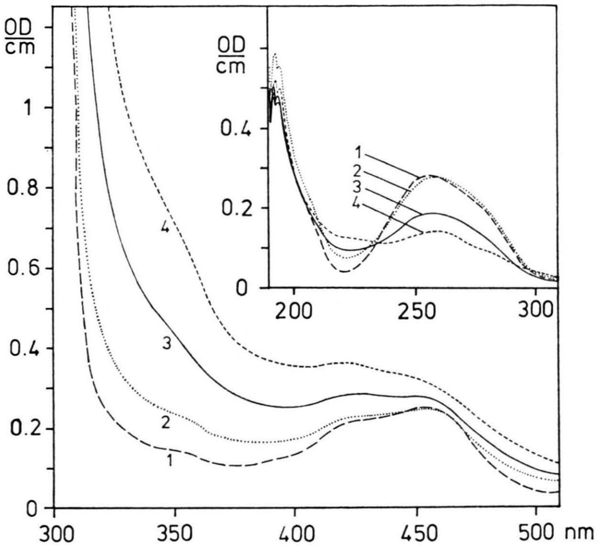

Fig. 2. Absorption spectra of the photoredoxsystem consisting of: 5×10^{-5} mol dm^{-3} Ru(bpy)$_3^{2+}$, 4×10^{-3} mol dm^{-3} MV^{2+} and 4×10^{-3} mol dm^{-3} EDTA before and after various irradiation periods: non-irradiated (1), irradiation time 2 h (2), 4 h (3) and 6 h (4). — *Insert*: The solution was diluted 250-times for absorption measurements below 300 nm.

3.6. *The Ru-complex/EDTA/MV^{2+} System with Catalyst*

In this series of experiments, the influence of PtO$_2$ (Adam's catalyst) on the hydrogen production and photochemical stability of the complex was investigated. The composition of the solutions and the concentration of the components were the same as above, but about 10 mg of PtO$_2$ catalyst were added to the solution. Irradiation conditions were not altered and the solution was thoroughly stirred during illumination. At the most favorable pH of 4.6, a hydrogen yield of 11×10^{-4} mol dm^{-3} h^{-1} was obtained for an illumination time of 45 min. This yield is by a factor of 2 higher than in the absence of catalyst. Absorption spectra were measured before and after every 2 h of irradiation and are presented in Figure 3.

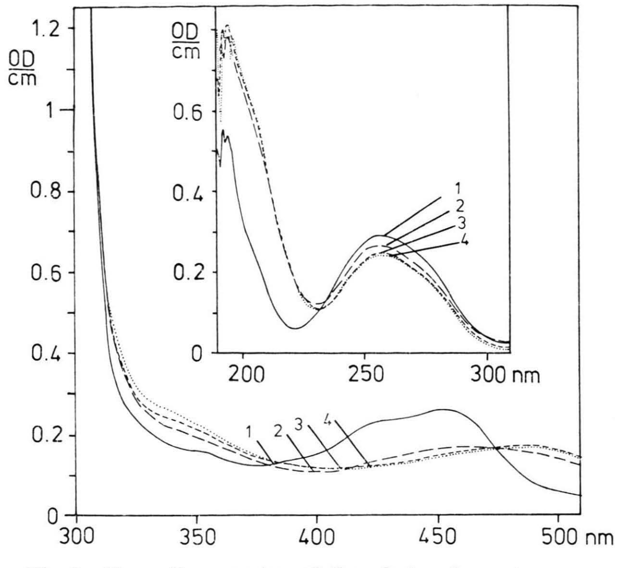

Fig. 3. Absorption spectra of the photoredoxsystem consisting of: 5×10^{-5} mol dm^{-3} $\mathrm{Ru(bpy)_3^{2+}}$, 4×10^{-3} mol dm^{-3} $\mathrm{MV^{2+}}$, 4×10^{-3} mol dm^{-3} EDTA and 10 mg $\mathrm{PtO_2}$ (as catalyst) before and after various irradiation periods: non-irradiated (1), irradiation time 2 h (2), 4 h (3) and 6 h (4). — *Insert*: The solution was diluted 250-times for absorption measurements below 300 nm.

4. Discussion

In contrast to previous results [4], it was established that the $\mathrm{Ru(bpy)_3^{2+}}$ complex in aqueous solution ($\mathrm{pH} = 6.5$) is photochemically unstable (Figure 1). Obviously, a scission of ligands occurs under prolonged u.v.-irradiation. Based on the changes of the measured absorption spectra it can be concluded that the at present non-identified products can undergo slow reactions when in contact with oxygen.

By comparing the $\mathrm{H_2}$ yield using the previously investigated system ($\mathrm{Ru(bpy)_3^{2+}/MV^{2+}/TEA}$) in the presence of $\mathrm{PtO_2}$ (Adam's catalyst) [11] with that obtained in the absence of a catalyst, it is evident that the latter one is essentially higher. Thereby a strong change of the absorption spectra in the range of 400–470 nm was observed in both cases, indicating a degradation of the ruthenium complex. In the presence of the catalyst an additional decrease of the absorption at $\lambda \sim 260$ nm occurs due to the photolysis of $\mathrm{MV^{2+}}$. The photochemical formation of hydrogen in this system can be explained by a previously postulated reaction mechanism [11], namely:

$$\mathrm{Ru(bpy)_3^{2+}} \xrightarrow{h\nu} [\mathrm{Ru(bpy)_3^{2+}}]^* , \tag{1}$$

$$[\mathrm{Ru(bpy)_3^{2+}}]^* + \mathrm{MV^{2+}} \rightarrow \mathrm{Ru(bpy)_3^{3+}} + \mathrm{M\dot{V}^{+}} , \tag{2}$$

$$\mathrm{Ru(bpy)_3^{3+}} + \mathrm{TEA} \rightarrow \mathrm{Ru(bpy)_3^{2+}} + \mathrm{TEA^{+}} , \tag{3}$$

$$\mathrm{M\dot{V}^{+}} + \mathrm{H^{+}_{aq}} \xrightarrow[\mathrm{PtO_2}]{} \mathrm{MV^{2+}} + \mathrm{H} , \tag{4}$$

$$\mathrm{H} + \mathrm{H} \rightarrow \mathrm{H_2} , \tag{5}$$

$k_5 = 1 \times 10^{10}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$ [19].

The evolution of H atoms according to reactions (4) and their recombination (5) was found to proceed only by a depletion of the electron donor (TEA), which regenerates the sensitizer, $\mathrm{Ru(bpy)_3^{2+}}$. The H atoms can naturally also attack each component of the system, which explains the observed degradation.

The $\mathrm{H_2}$ yield obtained in the absence of $\mathrm{PtO_2}$ is in contradiction to previous results [10, 11]. In order to explain this fact, one can assume that by illuminating the system under steady-state conditions, the $\mathrm{MV^{+}}$ radical cation, produced in surplus according to reaction (2), can be electronically excited ($\lambda_{\max} = 395$ nm and 600 nm [20]). This is underlined by the fact that the solution turns blue shortly after beginning illumination. Subsequently, the electronically excited $\mathrm{MV^{+}}$ is able to act as an electron donor by transfering an electron to $\mathrm{H^{+}_{aq}}$:

$$\mathrm{M\dot{V}^{+}} \xrightarrow{h\nu} [\mathrm{M\dot{V}^{+}}]^* , \tag{6}$$

$$[\mathrm{MV^{+}}]^* + \mathrm{H^{+}_{aq}} \rightarrow \mathrm{M\dot{V}^{2+}} + \mathrm{H} , \tag{7}$$

This process can occur as well with as without $\mathrm{PtO_2}$ catalyst. Further experiments are planned in order to explain the observed higher $\mathrm{H_2}$ value in the absence of a catalyst (Table 1).

The replacement of the electron donor by $\mathrm{SCN^-}$ gave no satisfactory results concerning the hydrogen yield, but only a small degradation of the system was observed. This indicates again that the higher $\mathrm{H_2}$ yield is accompanied by a strong destruction of the system. This confirms the formation of H atoms as intermediates and their reactivity with the substrates.

An interesting observation is the fact that $\mathrm{H_2}$ formation occurs not only by illuminating the Ru-complex in combination with $\mathrm{MV^{2+}}$ and EDTA in the presence of a Pt-catalyst [10], but also in its absence (Table 2). The formation of $\mathrm{H_2}$ in the second case is thereby very sensitive towards the acidity of the solution, showing a maximum yield at $\mathrm{pH} = 4.7$. In this case EDTA acts as an electron donor for the oxidized Ru-complex, which is regenerated:

$$\mathrm{Ru(bpy)_3^{3+} + EDTA \rightarrow Ru(bpy)_3^{2+} + EDTA^{+}}. \quad (8)$$

The formation of H_2 is therefore due to the consecutive reactions (1), (2), (6), (7) and (8). The pH influence on the H_2 yield using the analogous system (TEA as electron donor), but in the presence of the PtO_2 catalyst, has already been explained [11]. At lower pH values very fast back reactions are postulated, corroborated by flash photolysis experiments, whereas at higher pH values the potential of the reduction of H_{aq}^+ is shifted too far to the negative.

The changes of the absorption spectra caused by prolonged illumination of the Ru-complex/EDTA/MV^{2+} system in the absence of a Pt-catalyst (Fig. 2) show an essential decrease of the MV^{2+} concentration ($\lambda \sim 260$ nm). Also an increase of the OD-values in the range of 300–400 nm, probably due to photolytical products of MV^{2+}, can be seen.

By adding PtO_2 as a catalyst, the H_2 yield doubled (Table 2). At the same time, a relatively lower degradation of the system was observed (Figure 3). This is explainable by the fact that in addition to reaction (7), reaction (4) takes place. Also, the recombination of H atoms is facilitated by the catalyst, thus preventing photolytic processes to some extent.

Summarizing the results obtained in the absence and presence of PtO_2 as a catalyst in systems consisting of $Ru(bpy)_3^{2+}$, MV^{2+} and various electron donors (TEA, EDTA, SCN^-), a production of hydrogen by sensitized photolysis of water can occur. In all cases, however, relatively strong degradation processes were observed, whereby the presence of catalysts suppresses the depletion of MV^{2+} up to a certain extent. On the other hand, the donor is always used up whilst hydrogen is formed. It is further established that $M\dot{V}^+$ in its electronically excited state can act as an electron donor towards H_{aq}^+. All these investigated systems a still far from a practical use as a device for the photochemical production of hydrogen by means of solar energy. Further search for a more suitable electron donor is necessary.

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