Photoinduced Reduction of Water by Tin(IV) and Ruthenium(II) Porphyrins

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Abstract

In the paper are presented new photoredox systems for the reduction of water in which water-soluble Sn(IV) and Ru(II) porphyrins have been used as photosensitizers It has been found that during the photolysis of water Sn(IV) porphyrin underwent photoreduction whereas Ru(II) porphyrin underwent photooxidation. The successive photoproducts of Sn(IV) porphyrin in the reaction from EDTA were, first, Sn(IV) chlorin and, second, Sn(IV) bacteriochlorin. In the experiments on the photogeneration of hydrogen, a correlation between the rates of hydrogen evolution and the reduction potentials of the electron carriers has been observed. The highest rate of hydrogen generation by means of Sn(IV) and Ru(II) porphyrins has been found for those electron carriers whose values of reduction potentials were −0.55 and −0.45 V. In the case of Ru(II) porphyrin, the rate of hydrogen evolution additionally depended on the molecular structure of the electron carrier. It has been found that during the water photolysis, viologens show a tendency to form their respective complexes with Ru(II) porphyrin, but only when they occur in a one-electron reduced form in the solution.

Introduction

For a number of years research has been going on to find the optimum composition of photoredox systems for the decomposition of water into oxygen and hydrogen [1, 2]. In the case of photoreduction of water into hydrogen, three-component systems composed of photosensitizer (PS), electron carrier (C) and electron donor resolve water only when a suitable redox catalyst is present in the solution [3]. Platinum supported on a polymer base (Pt/PVA) [4] or a semiconductor base (Pt/TiO$_2$) [5] is usually used as the catalyst. However, the function of electron carrier is almost solely performed by the quaternary salts of 2,2′- and 4,4′-bipyridyl called viologens [3].

The efficiency of visible light energy conversion depends mainly on the physical and chemical pro-

perties of the photosensitizer. In other words, in the case of the photoreduction of water, the rate of hydrogen evolution depends mainly on quantum yield of excitation, and life-time and redox potential in excited state of the photosensitizer [6]. For this reason the porphyrins of Zn [7] Sn [8] and Pd [9] are more frequently used as photosensitizers, because they have most of required properties of a good photocatalyst. In connection with the above, it seems advisable to conduct investigations for the purpose of determining the photocatalytical activity of other metalloporphyrins.

In our studies, the following compounds were used for the first time as photosensitizers: 5,10,15, 20-tetra-*p*-(*N*-ethyl-*N,N*-dimethyl)aniliniumporphyrinato-bis-(hydroxide)tin(IV) disulphate [TEAPSn-(OH)$_2$], Fig. 1a, and 5,10,15,20-tetra-*p*-(N-ethyl-*N,N*-dimethyl)aniliniumporphyrinato-bis-(pyridine)-ruthenium(II) disulphate [TEAPRu(Py)$_2$] (Fig. 1b). The following viologens were used as electron carriers: *N,N*′-dibenzyl-4,4′-bipyridinium dichloride (BzVCl$_2$); *N,N*′-dicarboxymethylene-4,4′-bipyridinium dichloride (BetVCl$_2$); *N,N*′-diethyl-4,4′-bipyridinium dichloride (EtVCl$_2$); *N,N*′-dimethyl-4,4′-bipyridinium dichloride (MeVCl$_2$); *N,N*′-propylene-2,2′-bipyridinium dichloride (prVCl$_2$); *N,N*′-propylene-4,4′-dimethyl-2,2′-bipyridinium dichloride (MprVCl$_2$).

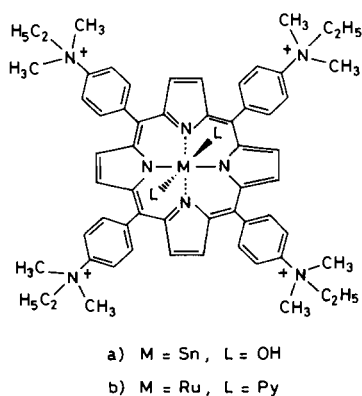Comparing the photocatalytical activities of TEAPSn(OH)$_2$ with TEAPRu(Py)$_2$, it has been found

Fig. 1. The structure of photosensitizers (a) TEAPSn(OH)$_2$, (b) TEAPRu(Py)$_2$.

on the basis of the rates of hydrogen evolution that TEAPRu(Py)$_2$ is the more active photosensitizer. In order to define more accurately the causes of the differences, spectroscopic studies were made within the visible range of the suitable prepared aqueous solutions of these metalloporphyrins. On the basis of the obtained spectroscopic data, the mechanisms of the processes of photoreduction of water into hydrogen by means of TEAPSn(OH)$_2$ and TEAPRu-(Py)$_2$, respectively, have been suggested.

Experimental

Synthesis

TEAPSn(OH)$_2$ was obtained by refluxing an equimolar methanolic solution of TEAPH$_2$ [10] and SnCl$_2$ (POCH, Gliwice) for one hour. The product was filtered and crystallized twice from methanol. The total yield was 80%.

Electronic spectra (H$_2$O): λ_{max} ($\epsilon \times 10^4$ M^{-1} cm^{-1}) = 420 (56.0), 556 (1.76), 595 nm (0.70). IR spectra (KRS-5): 1630, 1473, 1413, 1347, 1214, 1120, 1014, 920, 807 cm^{-1}. ^{1}H NMR spectra (CD$_3$-OD, HMDS)· δ = 9.28 (s, 8H), 8.46 (d, 16H), 3.92 (s, 24H), 3.55 (q, 8H), 1.10 (t, 12H).

TEAPRu(Py)$_2$ was synthesized according to the procedure described before [10]. Electronic spectra (H$_2$O). λ_{max} ($\epsilon \times 10^4$ M^{-1} cm^{-1}) = 421 (20.0), 532 (1.58), 567 nm (0.31). IR spectra (KRS-5). 1630, 1600, 1493, 1440, 1353, 1307, 1213, 1120, 1013, 914, 800 cm^{-1}. ^{1}H NMR spectra (CD$_3$OD, HMDS). δ = 9.10 (s, 8H), 8.43 (s, 16H), 3.93 (q, 8H + s, 24H), 1.43 (m, 10H), 1.17 (t, 12H).

BzVCl$_2$, BetVCl$_2$, EtVCl$_2$, MeVCl$_2$, prVCl$_2$, and MprVCl$_2$ were obtained during the quaternisation reaction [11] of 4,4'-bpy and 2,2'-bpy (POCH, Gliwice), and 4,4'-dimethyl-2,2'-bpy [12], respectively by BzCl, CH$_2$ClCOOH (POCH, Gliwice), (EtO)$_2$SO$_2$, (MeO)SO$_2$ (Fluka), and BrCH$_2$CH$_2$-CH$_2$Br (POCH, Gliwice). Pt/PVA was prepared using Gratzel's method [4]. The sodium salt of ethylenediaminetetraacetic acid (EDTA) was purchased from POCH, Gliwice.

Experimental Procedure

Hydrogen was generated in a cell of an internal vessel, Fig. 2, made of Termisil glass of the dimensions. diameter 25 mm, height 60 mm, with a side arm. In all the experiments, the cell was filled with a volume of reaction mixture (25 cm^3) sufficient to submerge the thermometer thread in the liquid. After 15 min degassing of the solution by means of argon, the cell was irradiated from a slide projector with 150 W halogen lamp. During irradiation the contents of the cell were magnetically stirred (200 r.p.m.) and kept at constant temperature (30 ± 1 °C) by means of water jacket.
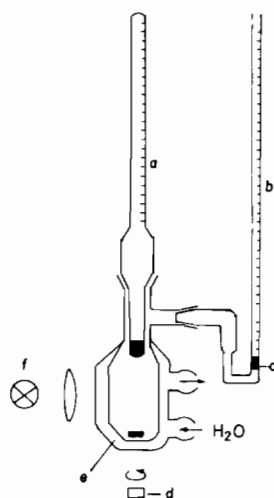

Fig. 2 Schematic view of the cell (description in 'Experimental' section) (a) thermometer, (b) side arm, internal diameter 3 mm, length 30 cm, (c) one cm-high water layer, (d) magnetic stirrer; (e) water jacket, (f) 150 W halogen lamp from a slide projector.

The volume of hydrogen generated during irradiation was registered by means of the movement of a one cm high water layer in the side arm of the cell. In all the experiments, the composition of the reaction mixture was as follows 10^{-4} M photosensitizer, 0.005 M electron carrier, 0.01 M EDTA, 2 M acetate buffer (pH 5), and 0.5 cm^3 of Pt/PVA. Triple-distilled water was used for making the solutions.

Apparatus

Absorption spectra within the visible range were recorded by means of a SPECORD UV-Vis (Carl Zeiss, Jena) spectrophotometer. In order to obtain the spectral changes following irradiation of the solutions of suitable photoredox systems, the spectrophotometrical cell filled with the respective solution was irradiated by means of a slide projector with a 150 W halogen lamp with a pause every half minute. During those pauses the absorption spectra of the solution in the cell were registered. The reactions were carried out at a temperature of 20 ± 1 °C and in argon atmosphere.

The hydrogen gas evolved during the photolysis was checked by means of a GHF 18.3 (Chromatron, Berlin) gas chromatograph, column: chromosorb 102, 2 mm, 50 °C, carrier gas He.

The ^{1}H NMR measurements were performed by means of a Varian XL-100 spectrometer.

The IR spectra were obtained by means of a SPECORD 75 IR (Carl Zeiss, Jena) spectrophotometer using the ATR technique and a reflection element made from KRS-5.

Results and Discussion

Sensitized Photoreduction of Water by TEAPSn-(OH)$_2$

One of the methods which makes it possible to observe the reactions undergone by metalloporphyrins during photoredox processes is the registering of absorption spectra of the reaction mixture irradiated by the visible light depending on the time of exposure. This method is especially useful in investigating the reactions occurring during the photolysis of water [1] because the photosensitizer as well as the intermediate products participating in the process of electron transition have characteristic absorption bands within the visible range.

In order to find out whether TEAPSn(OH)$_2$ during irradiation is subject to reduction by EDTA in acidic medium, and also whether the possible products of the photoreduction of TEAPSn(OH)$_2$ are capable of reducing viologens, the spectral changes following irradiation of an aqueous solution which contained 3.09×10^{-5} M TEAPSn(OH)$_2$, 0.001 M EDTA and 2 M acetate buffer (pH 5) were determined before and after the addition of MeVCl$_2$. Before irradiation and before the addition of MeVCl$_2$, the absorption spectrum of this solution was composed of bands characteristic for TEAPSn(OH)$_2$ [10]. However, during the 15 min irradiation two successive qualitative changes were found in the absorption spectrum of this solution (Fig. 3). First, gradual decay of the peak at $\lambda = 556$ nm and a rise of peak at $\lambda = 625$ nm were observed (Fig. 3a) and then, after 9 min irradiation, an increase of the absorbance of the new band at $\lambda =$
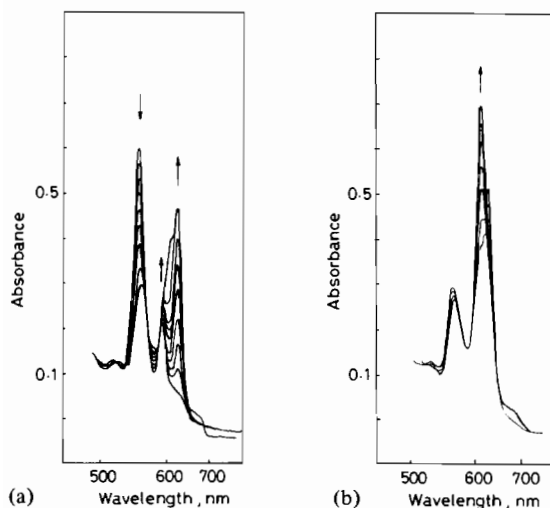
610 nm was found (Fig. 3b). The secondary spectral changes needed only 4 min of irradiation. The continuation of irradiation did not cause further changes in the absorption spectrum of the solution studied. Changes did not take place after switching off the light nor after adding MeVCl$_2$ or Pt/PVA to the solution. However, an addition of MeVCl$_2$ together with resuming the exposure to light caused immediate decay of the band at $\lambda = 610$ nm with the simultaneous appearance of two peaks at $\lambda = 625$ and 605 nm, Fig. 4. The increase of the band at $\lambda = 605$ nm with the time of irradiation, Fig. 4c, testifies to photogeneration of the cation radicals of MeVCl$_2$ (MeV$^{\cdot +}$) [8, 11, 13].
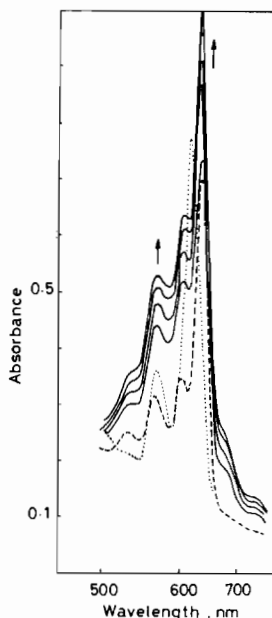

Fig. 4. Spectral changes following irradiation of outgassed aqueous solution of TEABSn(OH)$_2$ (3.09×10^{-5} M) containing EDTA (0.001 M), 2 M acetate buffer (pH 5), and MeVCl$_2$ (1.5×10^{-4} M). Light exposure time: (a) 0 ($\cdots\cdots$) (b) 1 min (------); (c) 4, 6, 8 and 10 min (———).

On the basis of these spectroscopic studies and literature data [8, 14], it may be stated that TEAPSn(OH)$_2$ in an acidic medium under the effect of light is subject to a two-stage reduction by EDTA, Fig. 5. First, the photoexcited TEAPSn(OH)$_2$ undergoes a two-electron reduction to tin(IV) chlorin [TEACSn(OH)$_2$], **III**, after which it undergoes a second two-electron photoreduction to tin(IV) bacteriochlorin [TEABSn(OH)$_2$], **V**. Tin(IV) phlorin, **II**, and tin(IV) chlorinophlorin, **IV**, are probably intermediate products of the photoreduction. The fact that they were not found in the reaction mixture during spectroscopic studies suggests that they undergo rapid rearrangement immediately after formation, giving TEACSn(OH)$_2$ and TEABSn(OH)$_2$, respectively. In view of the above, the absorption
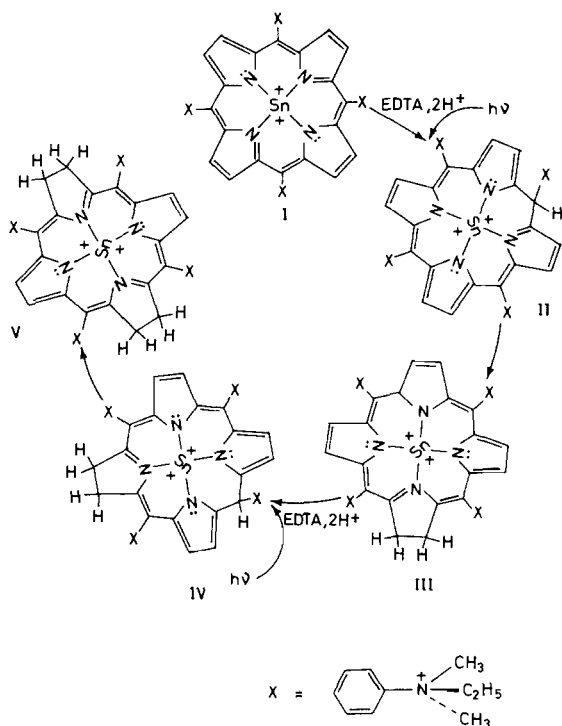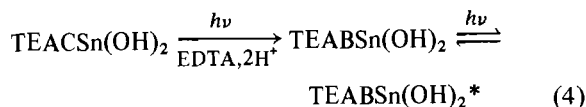

Fig. 3. Spectral changes following irradiation of aqueous solution of TEAPSn(OH)$_2$ (3.09×10^{-5} M) containing EDTA (0.001 M) and 2 M acetate buffer (pH 5). Absorption spectra were recorded after irradiation for (a) 0, 1, 2, 3, 4, 5, 6, 7, 8 and 9 min; (b) 9, 9.5, 10, 10.5, 11, 11.5, and 12 min, respectively, by means of 150 W halogen lamp, at 20 ± 1 °C.

Fig. 5. Proposed mechanism of the photoreduction of TEAP-Sn(OH)$_2$ by EDTA.

$$\text{TEACSn(OH)}_2 \xrightarrow[\text{EDTA,2H}^+]{h\upsilon} \text{TEABSn(OH)}_2 \xrightleftharpoons{h\upsilon}$$

$$\text{TEABSn(OH)}_2{}^* \qquad (4)$$

$$2\text{C}^- + 2\text{H}^+ \xrightarrow{\text{Pt}} 2\text{C} + \text{H}_2 \qquad (5)$$

If the presented mechanism is true, it may be expected that the rate of hydrogen evolution will depend on the reduction potential of the electron carriers (E_{C/C^-}). In other words, the rate of hydrogen evolution will be highest for the particular electron carrier with a reduction potential E_{C/C^-}^m found within the range $E_{PS^*/PS^+} < E_{C/C^-}^m < E_{H/H^+}$ [13], where E_{H/H^+} denotes an overpotential of hydrogen evolution on Pt at the pH of reaction mixture and E_{PS^*/PS^+} denotes the redox potential of PS in excited state. The redox potential effect of the electron carriers on the rate of hydrogen evolution was studied for the following viologens: BzVCl$_2$, BetVCl$_2$, MeV-Cl$_2$, prVCl$_2$, and MprVCl$_2$. Their E_{C/C^-} values according to [11] are -0.34, -0.44, -0.45, -0.55, and -0.69 V, respectively. For all the viologens the rates of hydrogen evolution were different, and they were correlated with the redox potential of viologens, Fig. 6. The maximum rate of hydrogen production was found at $E_{C/C^-}^m = -0.60$ V, Fig. 7a.

On the basis of the curve profile in Fig. 7a one cannot univocally state that the rate of hydrogen evolution is controlled only by the redox effect of viologens. In other words, if the process of photo-reduction of water sensitized by TEAPSn(OH)$_2$ was controlled by the rate of the oxidative quenching reaction (3), then the curve in Fig. 7a should exhibit a sharp maximum. In the mechanism of photoreduction of water proposed by us, reactions
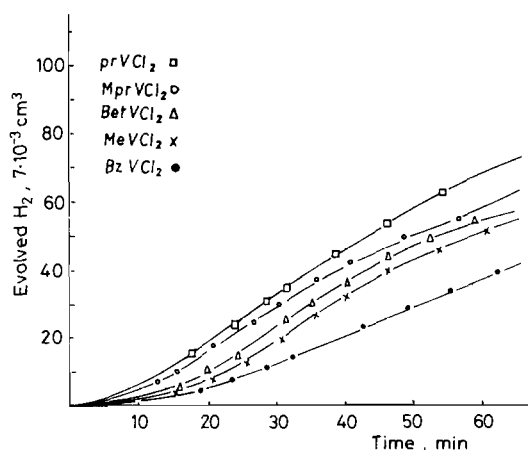
bands at $\lambda = 625$ and 610 nm observed in the particular stages of photoreduction of TEAPSn(OH)$_2$ came from the absorption of the successively photo-produced TEACSn(OH)$_2$ and TEABSn(OH)$_2$.

It should be noted that the obtained photo-products of TEAPSn(OH)$_2$ in their ground states showed great resistance to oxygen from the air and were not oxidized in the presence of MeVCl$_2$ and Pt/PVA. TEABSn(OH)$_2$ in the light-excited state showed special activity in the reduction of viologens. It may then be concluded that TEABSn-(OH)$_2$ may serve as photosensitizer in photoredox systems for the reduction of water, since the redox potential of MeVCl$_2$ is sufficiently low to reduce water in the presence of Pt [3].

On the basis of the discussion presented above, it may be stated that the mechanism of photogeneration of hydrogen from water by means of photoredox systems obtained on the basis of TEAPSn-(OH)$_2$ involves the following reactions:

$$\text{TEAPSn(OH)}_2 \xrightarrow[\text{EDTA,2H}^+]{h\upsilon} \text{TEACSn(OH)}_2 \xrightarrow[\text{EDTA,2H}^+]{h\upsilon}$$

$$\text{TEABSn(OH)}_2 \qquad (1)$$

$$\text{TEABSn(OH)}_2 \xrightleftharpoons{h\upsilon} \text{TEABSn(OH)}_2{}^* \qquad (2)$$

$$\text{TEABSn(OH)}_2{}^* + 2\text{C} \longrightarrow \text{TEACSn(OH)}_2 + 2\text{C}^- + 2\text{H}^+ \qquad (3)$$

Fig. 6. Time dependence of hydrogen evolution as a function of different electron carriers for the samples (25 cm^3) containing TEAPSn(OH)$_2$ (1.06 × 10^{-4} M), EDTA (0.01 M), 2 M acetate buffer (pH 5), Pt/PVA (0.5 cm^3) and respective viologen (5 × 10^{-3} M), irradiated by means of 150 W halogen lamp, at 30 ± 1 °C.
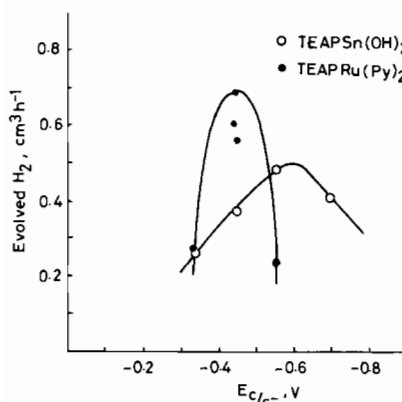
Fig. 7. Effect of the reduction potential of electron carriers on the rate of hydrogen evolution for the photoredox systems based on (a) TEAPSn(OH)$_2$, —o—; (b) TEAPRu(Py)$_2$, —●—, respectively.

Fig. 8. Spectral changes following irradiation of aqueous solution of TEAPRu(Py)$_2$ (5.06 × 10^{-5} M) containing EDTA (0.001 M), 2 M acetate buffer (pH 5) and EtVCl$_2$ (1.4 × 10^{-4} M). Absorption spectra were recorded after irradiation for (a) 0 min, ------; (b) 1,2,3,4,5 and 6 min, respectively, ——; by means of 150 W halogen lamp at 20 ± 1 °C and in argon atmosphere.

(1)–(5), the process of photogeneration of viologen cation-radicals has the character of consecutive reactions, that is, reaction (3) is preceded by reaction (4). It may be that the weak dependence between the rate of hydrogen evolution and the reduction potential of electron carriers, Fig. 7a, is the consequence of reaction (4), which determines the rate of regeneration of the photoactive form of TEAB-Sn(OH)$_2$ and the yield of reaction (3).

Sensitized Photoreduction of Water by TEAPRu-(Py)$_2$

A characteristic feature of some metalloporphyrins is the formation of respective complexes with viologens [7c, 9]. During the photolysis of water, they facilitate the process of electron transfer, thus increasing the effectiveness of conversion of light energy. The process of formation of the metalloporphyrin-viologen complex may be ascertained after adding suitable viologen to the solution on the basis of the decreasing peaks and red shift characteristic to metalloporphyrin.

In our studies, no changes in the absorption spectrum of an aqueous solution of TEAPRu(Py)$_2$ was found after adding any of the following viologens: EtVCl$_2$, MeVCl$_2$, BetVCl$_2$, prVCl$_2$. In aqueous solution TEAPRu(Py)$_2$ exists in the form of a tetra-cation, Fig. 1b; for this reason, the force of electrostatic repulsion between TEAPRu(Py)$_2$ and dications of the viologens does not allow these ions to approach close enough for the formation of CT bands. In relation to the above, the formation of TEAPRu(Py)$_2$–viologen complex is not very likely.

In order to determine the chemical activity of TEAPRu(Py)$_2$ in excited state, spectroscopic studies were carried out in the visible range of an aqueous solution which contained 5.06 × 10^{-5} M TEAPRu-(Py)$_2$, 0.001 M EDTA, 2 M acetate buffer (pH 5),
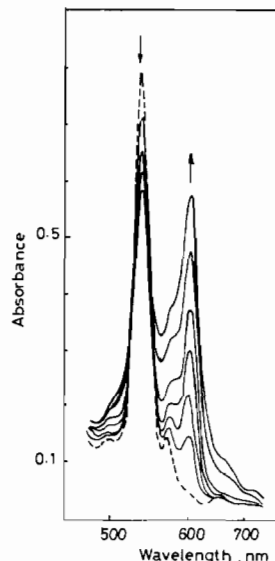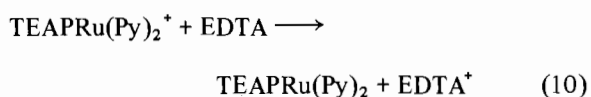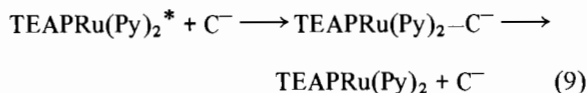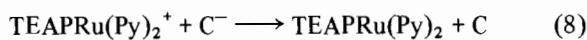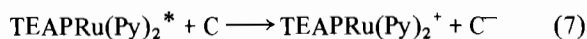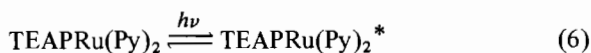
and 1.4 × 10^{-4} M EtVCl$_2$. The spectral changes following irradiation of this solution consisted of a gradual decrease of the TEAPRu(Py)$_2$ peak in the band at $\lambda = 532$ nm and the inducing of the absorption at $\lambda = 605$ nm, Fig. 8. The decrease of absorption at $\lambda = 532$ nm ceased after 4 min irradiation; however, the peak at $\lambda = 605$ nm increased with the time of exposure.

From the spectroscopic data presented above, it appears that TEAPRu(Py)$_2$, similarly to TEAPSn-(OH)$_2$ easily reduced EtVCl$_2$ to EtV$^{\cdot+}$ after irradiation and in the presence of EDTA. However, the product of TEAPRu(Py)$_2$ photooxidation, unlike TEACSn(OH)$_2$, was not found in the reaction mixture since immediately after its formation it was reduced by EDTA. The decrease of the absorption band of TEAPRu(Py)$_2$ at $\lambda = 532$ nm during irradiation and in the presence of EtV$^{\cdot+}$ suggests that TEAPRu(Py)$_2$–EtV$^{\cdot+}$ complex was formed. In this case, the formation of metalloporphyrin-reduced viologen complex is especially preferred on account of the possibility of formation of a bond between these ions at the cost of free electrons, which are found in viologen cation-radicals as well as in TEA-PRu(Py)$_2$ after excitation by light. Similar spectral changes in the solution at $\lambda = 532$ nm were also observed when other viologens were used in place of EtVCl$_2$.

From the above discussion, it appears that the mechanism of photoreduction of water by means

of photoredox systems based on TEAPRu(Py)$_2$ consists of the following reactions:

$$TEAPRu(Py)_2 \overset{h\nu}{\rightleftharpoons} TEAPRu(Py)_2{}^* \qquad (6)$$

$$TEAPRu(Py)_2{}^* + C \longrightarrow TEAPRu(Py)_2{}^+ + C^- \qquad (7)$$

$$TEAPRu(Py)_2{}^+ + C^- \longrightarrow TEAPRu(Py)_2 + C \qquad (8)$$

$$TEAPRu(Py)_2{}^* + C^- \longrightarrow TEAPRu(Py)_2 - C^- \longrightarrow$$

$$TEAPRu(Py)_2 + C^- \qquad (9)$$

$$TEAPRu(Py)_2{}^+ + EDTA \longrightarrow$$

$$TEAPRu(Py)_2 + EDTA^+ \qquad (10)$$

$$C^- + H^+ \overset{Pt}{\longrightarrow} C + 0.5 H_2 \qquad (11)$$

In order to determine the correlation between the rate of hydrogen evolution from water sensitized by TEAPRu(Py)$_2$ and the reduction potentials of electron carriers, experiments of photogeneration of hydrogen using five photoredox systems were performed, in which the viologens BzVCl$_2$, BetVCl$_2$, EtVCl$_2$, MeVCl$_2$, and prVCl$_2$ were used as electron carriers. For each of the photoredox systems used, different rates of hydrogen evolution were observed, Fig. 9. From the curve in Fig. 7b, it may be seen that these differences result, first of all, from the electro-chemical properties of electron carriers used. Moreover, from the maximum of this curve, the optimum value of the potential E_{C/C^-} for the rate of hydrogen evolution was determined to be $E_{C/C^-}^m = -0.45$ V.

The redox effect of viologens on the rate of hydrogen generation (eqn. 11) from water was not the only and finally-decisive one. For MeVCl$_2$,
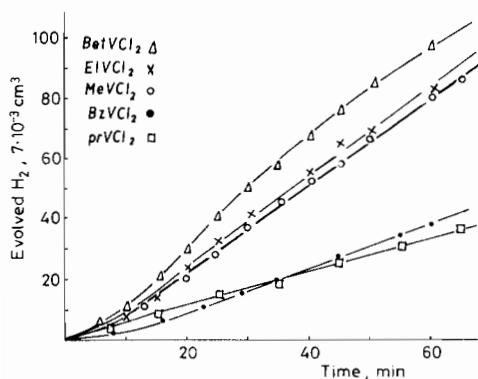

Fig. 9. Time dependence of hydrogen evolution as a function of different electron carriers for samples (25 cm^3) containing TEAPRu(Py)$_2$ (1.05×10^{-4} M), EDTA (0.01 M), 2 M acetate buffer (pH 5), Pt/PVA (0.5 cm^3), and respective viologen (5×10^{-3} M), irradiated by means of 150 W halogen lamp, at 30 ± 1 °C.

EtVCl$_2$, and BetVCl$_2$, the results of the photoreduction of water were clearly different from each other, Fig. 9, though the potentials E_{C/C^-} for these viologens are almost the same and equal to -0.45 ± 0.01 V [11]. The sequence in the rate of hydrogen evolution of these compounds was as follows: BetVCl$_2$ > EtVCl$_2$ > MeVCl$_2$. It could then be suggested that in the case when E_{C/C^-} is close to E_{C/C^-}^m, the yield of reaction (7) determines the physical-chemical quantities whose values depend on the molecular structure of the reagents, i.e., on the probability of meeting (collision) of the photosensitizer with the electron carrier and on the yield of ions separation after the electron transfer in the encounter complex [15].

The separation of the reaction products after electron transfer (7) and the blockade of the back reaction (8) were probably facilitated by the previously described process of the formation of complexes between TEAPRu(Py)$_2$ and the reduced form of viologens, since the reaction of complexation (9) occurs directly after the reduction of the electron carrier. In other words, the greater the equilibrium constant of this complex formation, the greater is the yield of ions separation after the electron transfer.

The molecular structures of the electron carriers used are similar to each other with the exception of BetVCl$_2$ which, unlike MeVCl$_2$ and EtVCl$_2$, has two negatively-charged carboxylic groups. In connection with the above, tetracations of TEAPRu(Py)$_2$ in aqueous solution repulse the dications of MeVCl$_2$ and EtVCl$_2$ more easily than the betaine ions of BetVCl$_2$; i.e., the probability of the meeting of TEAPRu(Py)$_2$ with BetVCl$_2$ and thus the probability of the occurrance of reaction (7) for BetVCl$_2$ is the highest, in comparison to the remaining viologens.

It can then be proposed that the differences in the values of the equilibrium constants for the formation of the respective encounter complexes of reaction (7) are responsible for the observed differences in the rates of hydrogen generation by means of BetVCl$_2$ in comparison with MeVCl$_2$ and EtVCl$_2$.

Conclusion

Based on TEAPSn(OH)$_2$ and TEAPRu(Py)$_2$, photoredox systems for the photoreduction of water to hydrogen have been developed. During the photolysis of water, the systems undergo a series of reactions (1)–(5) and (6)–(11), respectively. It has been found that the hydrogen evolution rates correlate with the redox potential of the electron carriers, with the maximum hydrogen production for $E_{C/C^-} = -0.60$ and -0.45 V for TEAPSn(OH)$_2$ and TEAPRu(Py)$_2$, respectively. Complex

formation was observed between TEAPRu(Py)$_2$ and the cation-radicals of viologens. The formation of these complexes during the photolysis of water probably facilitates the separation of the reaction products of the oxidative quenching of the fluorescence of TEAPRu(Py)$_2$ by the viologens. The rate of hydrogen evolution in the case of TEAPRu(Py)$_2$ depends additionally on the molecular structure of the viologens, and it was highest for BetVCl$_2$.

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